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Analytical Support, Characterization, and Optimization of a Canine Training Aid Delivery System: Phase 2

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14. ABSTRACT

The objective of the second phase of the study was to analytically evaluate the newly developed Mixed Odor Delivery Device (MODD) and compare the device to the Merger, a previously designed apparatus for the delivery of explosive odorants to canines. Additionally, the odor profiles of homemade explosive (HME) materials, mixed and unmixed, were evaluated as a means for experimentally validating the use of the Merger or MODD. The design of the MODD was also assessed with trained detector canines. Results of these preliminary canine trials informed the final design of the device. Additional laboratory testing confirmed the efficacy of these design modifications. Finally, a formal set of canine trials substantiated the previous canine trials and analytical evaluations.

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EXECUTIVE SUMMARY

Homemade explosives (HMEs), often used in improvised explosive devices (IEDs), are most commonly composed of simple binary explosive mixtures, such as ammonium nitrate (AN) or potassium chlorate (PC) combined with various fuel sources. Though many devices exist for the detection of explosives, canines continue to be the most effective tool both at home and abroad, particularly for the detection of HMEs. The main challenge to training canines to detect HMEs is safety. Mixed explosives are difficult to safely obtain, store, and transport, and training is thus frequently limited by same-day production requirements and oversight by certified chemists.

To address these challenges a device referred to as the Merger was previously designed. The HME components are housed in separate compartments of the Merger, requiring no additional safety precautions. The HME odor is then sampled by the canine at the outlet as a mixture representing the odor of the mixed explosive materials.

Results from the Phase 1 study demonstrated that the Merger could be used to produce mixed odor profiles from separated components, and based on the results of these analyses, an improved odor delivery device, referred to as the Mixed Odor Delivery Device, or MODD, was designed, evaluated, and fabricated. The modified design preserved the advantageous features of the Merger, and improved upon it by incorporating a more compact design, reducing training aid mass requirements, and adding the ability to vary component ratios and total outlet vapor concentration without change in the mass of the analyte.

The objective of the second phase of the study was to further evaluate the MODD in comparison to the Merger. In phase 1, computational modeling demonstrated that the vapor distribution of DNT is similar in the Merger and MODD while using less analyte material in the MODD. Laboratory results have confirmed this to be true for several analytes. Experiments were then carried out to assess the mixing of multiple vaporous components in the MODD and Merger, focusing on variables affecting the vapor ratio output. Results again showed similarity in the vapor distribution between the Merger and MODD, and when vapor ratios were compared to the headspace from an alternate container or to calculated values, the vapor profiles were statistically the same to that in the MODD. The MODD thus accurately portrays the mixed odor of these separated compounds. This work was extended to HME components in the MODD, and it was shown that holding the components in the MODD does not alter the odor profile. Overall

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this implies that the separated components in the MODD will portray an accurate mixed odor for canine training.

Additionally, the odor profiles of homemade explosive (HME) materials, mixed and unmixed, were evaluated without use of the MODD or Merger as a means for experimentally validating the use of the Merger or MODD. As the purpose of the MODD or Merger was to represent mixed odor from unmixed component sources, it is imperative to determine if the physical mixing of these components altered the presentation or make up of the odor profile. The results for mixed and unmixed components were shown to be similar, supporting the training of canines using such a device.

Using the MODD prototype design established in Phase 1, ten additional devices were fabricated allowing for canine trials. Results of the preliminary canine trials informed the final design of the device, and additional laboratory testing confirmed the efficacy of these design modifications. In the final set of trials the canines located the MODD containing both of the separated components of the HME (ammonium nitrate/fuel oil) at the same rate as when containing the mixed material. Canines located the MODDs containing only the single components at a significantly lower rate. This formal set of canine trials substantiated the previous canine trials and analytical evaluations that the MODD design accurately portrays the vapor profile of mixed explosives from separated components.

OBJECTIVE

The objective of the second phase of the study was to analytically evaluate the newly developed Mixed Odor Delivery Device (MODD) and compare the device to the Merger, a previously designed apparatus for the delivery of explosive odorants to canines. Additionally, the odor profiles of homemade explosive (HME) materials, mixed and unmixed, were evaluated as a means for experimentally validating the use of the Merger or MODD. The design of the MODD was also assessed with trained detector canines. Results of these preliminary canine trials informed the final design of the device. Additional laboratory testing confirmed the efficacy of these design modifications. Finally, a formal set of canine trials substantiated the previous canine trials and analytical evaluations.

BACKGROUND

Homemade explosives (HMEs), often used in improvised explosive devices (IEDs), are most commonly composed of simple binary explosive mixtures, such as ammonium nitrate (AN) or potassium chlorate (PC) mixed with various fuel sources. Ammonium nitrate and potassium chlorate can both be either legally obtained or easily purified from commercial substances. When these oxidizers are combined with fuel sources, such as aluminum, fuel oil, or sugar, for example, the resulting mixtures are highly explosive.

Though many devices exist for the detection of explosives, canines continue to be the most effective tool both at home and abroad, particularly for the detection of HMEs. In 2012, the Office of Naval Research deployed as many as 280 IED Detector Dogs (IDDs) to Afghanistan [1]. These canines were vital in protecting marines from IED detonations during the course of their mission.

The main challenge to training canines on HMEs is safety. Mixed explosives are difficult to safely obtain, store, and transport, and training is thus frequently limited by same-day production requirements, with strict use and disposal oversight by explosive chemists. These safety measures are costly and time consuming; thus limiting the frequency of training exercises, and leading many canine/handler teams to train on the oxidizer alone instead of the explosive mixture. Training on mixtures has proven to be important as studies with trained canines have shown that canines trained on AN alone do not reliably detect the mixture of AN and aluminum (Al) [2]. An additional study using PC and several different fuels yielded similar results [3].

To address these challenges the Merger [4] was originally designed for the purpose of canine odor recognition training [2] [3]. Binary explosive components are placed in separate compartments of the Merger, requiring no additional safety precautions. The lower portion of the Merger housing the separated components, is made up of two tubes (PVC pipe). The tubes are connected by a tee leading to a cup with a grating (PVC drain fitting) as the outlet. The separated odor vapors mix as they diffuse through the tee to the outlet, where the canine samples the combined component odors (Figure 1). The HME odor is sampled by the canine at the outlet as a mixed odor representing the odor of the mixed explosive materials. The outlet was conceived to localize the odor and minimize loss due to permeation to the environment.

Figure 1. Image of the Merger, an odor delivery device used for canine training exercises **[3]**.

Results from the Phase 1 study demonstrated that the Merger could be used to produce mixed odor profiles from separated components [5], and these odors were recognizable to trained canines [2]. The vapor distribution of a surrogate compound, 2,4-dinitrotoluene (2,4-DNT), was examined using both laboratory and computational analyses. Results revealed a symmetric vapor distribution at the outlet with a greatly decreased vapor concentration compared to that at the source. The decrease in vapor concentration throughout the body of the Merger resulted from the dilution of vapor into the large internal volume of the Merger, in addition to the likely absorption of the compound vapors to the PVC material surface. This symmetric distribution implies suitable mixing of the component vapors at the Merger outlet, while the reduced vapor concentration suggests that little analyte vapor was lost to the surrounding environment.

Based on the results of these analyses, an improved odor delivery device, referred to as the Mixed Odor Delivery Device, or MODD, was designed, evaluated, and fabricated (Figure 2). The modified design preserved the advantageous features of the Merger and improved upon it by incorporating a more compact design, reducing training aid mass requirements, and the ability to vary component ratios and total outlet vapor concentration (using restrictor plugs; Figure 3) without change in the mass of the analyte [5] (Figure 4).

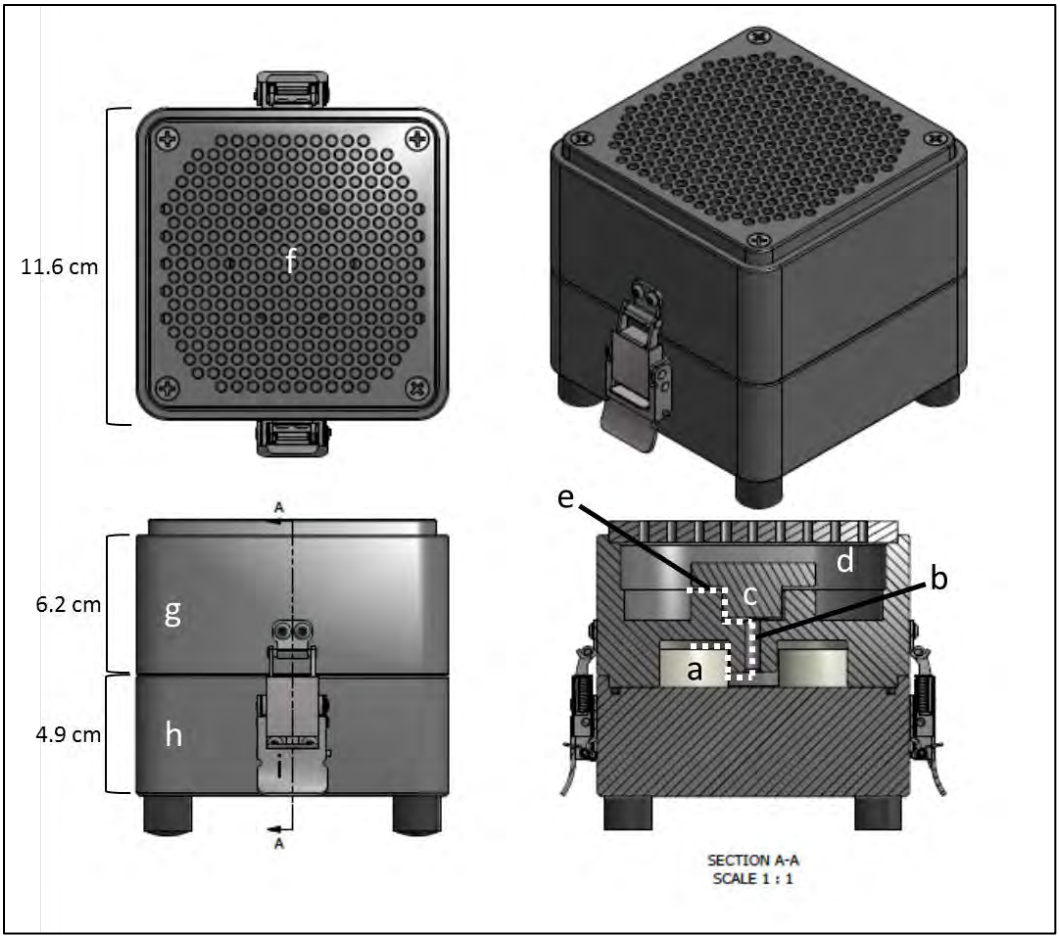


Figure 2. Diagram of the Mixed Odor Delivery Device (MODD); a) one of four compartments for analyte vials, b) neck within which analyte odors mix and diffuses towards outlet, c) restrictor plug used to decrease total vapor concentration, d) upper mixing chamber beneath MODD outlet, e) space under restrictor plug for vapors to diffuse, f) grating at outlet, g) upper chamber, h) lower chamber, i) clasp creating seal between upper and lower chambers.

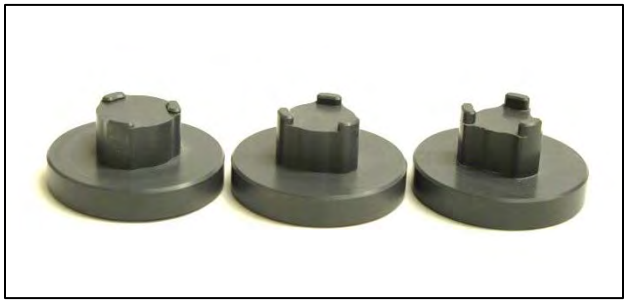


Figure 3. Photo of restrictor plugs of various sizes used to reduce total output of vapor from the MODD. Size of "feet" on plugs allows more or less vapor to be released.

Figure 4. Photo of Mixed Odor Delivery Device (MODD) with grating and restrictor plug removed.

Phase 2 of this research project focused on further mixing characterization of the MODD by means of both surrogate compounds, as well as actual HME materials. Using the prototype design established in Phase 1, ten additional devices were fabricated allowing for canine trials. Preliminary canine trials informed minor modifications to the final design. The final design was then further evaluated in the laboratory and a concluding set of canine trials were carried out.

In addition, the odor profiles of HME materials, mixed and unmixed, were analytically compared using three methods of delivery, a headspace sampling chamber or vial alone, the Merger, or the MODD. The results for mixed and unmixed components were shown to be similar, supporting the training of canines using such a device.

TECHNICAL APPROACH, RESULTS, AND DISCUSSION

Field and Laboratory Evaluation of homemade explosives (HMEs)

Evaluation of ammonium nitrate and aluminum (AN-Al) training aids

Method - Fresh and aged AN-Al canine training aids were evaluated analytically using a variety of methods. The training aids consisted of 113 g of AN-Al. The ammonium nitrate was purchased in prill form (GFS Chemcal; Powell, OH) then ground prior to mixing with the Al.

The aluminum flake used was supplied by Toyal America Inc. (ATA 7100 leafing flake with stearic acid; Lockport, IL). AN and Al were mixed at a 12:1 ratio. The aids were contained in 5"x 3" cloth drawstring bags (Midwest Pacific; Spokane, Washington), which were placed in 1 gallon paint cans (Tri-Tech Forensics; Southport, NC). Lids with holes drilled to fit the sampling devices were placed over the paint cans. Sampling methods included headspace extraction by solid phase microextraction (SPME), with analysis by gas chromatography / mass spectrometry (GC/MS). Additionally, vaporous ammonia was collected using passive sampling with sorbent pads and analysis by ion chromatography (IC).

SPME (Sigma-Aldrich; St. Louis, MO) is an extraction device for volatiles and semi-volatiles in headspace or in solution. The SPME apparatus consists of a fused-silica fiber coated with an absorbent polymer. Analyte extraction is a result of the partitioning of vaporous species between the vapor phase and the fiber coating. Following extraction, analytes were desorbed from the fiber by thermal desorption into the inlet of an Aglient 6890 GC with a 5799 MSD (Agilent Technologies; Santa Clara, CA). A polydimethylsiloxane/divinylbenzene/carboxen (PDMS/DVB/CAR) (Sigma-Aldrich) absorbent fiber polymer was used for the extractions throughout all experiments. For this investigation, an extraction time of four hours was chosen. For sampling, the SPME fiber was inserted in to the headspace of the can following a one hour equilibration of the training aid in the can. The fibers were returned to the laboratory for same-day analysis. Analytes were thermally desorbed in the GC inlet at 250 ˚C. The temperature program of the GC column oven begun at 60 ˚C, then was increased to 175 ˚C at 40 ˚C/min, increased again to 240 ˚C at 30 ˚C/min, and finally held for 5 min. A 30 m x 0.32 mm i.d. Rtx-Volatiles Amine column (Restek, Inc.; Bellefonte, PA) was used. The column flow was 2 mL/min with an inlet split of 10:1. The mass scan range of the MS was 30-220 m/z.

Ammonia, a vaporous degradation product of AN, is difficult to collect and detect by traditional SPME-GC/MS. For this reason Ogawa passive ammonia samplers (Ogawa Co.; Pompano Beach, FL) were utilized. The passive samplers (Figure 5), containing sorbent pads pre-coated for ammonia absorption, were placed into the can with the AN-Al training aids for five hours. Upon returning to the laboratory, the sorbent pads were removed from the sampling device and extracted with deionized water. The water was then analyzed by ion chromatography using a Dionex ICS 5000IC (Thermo Scientific; Sunnyvale, CA). The injection volume was 0.4 µL, and the separation was performed under isocratic and isothermal (30 ^{o}C) conditions. 20 mM

methanesulfonic acid eluent was pumped through a Dionex CS12a cation exchange column (Thermo Scientific) at 10 µL/min. Quantification was carried out by comparison to external calibration curves.

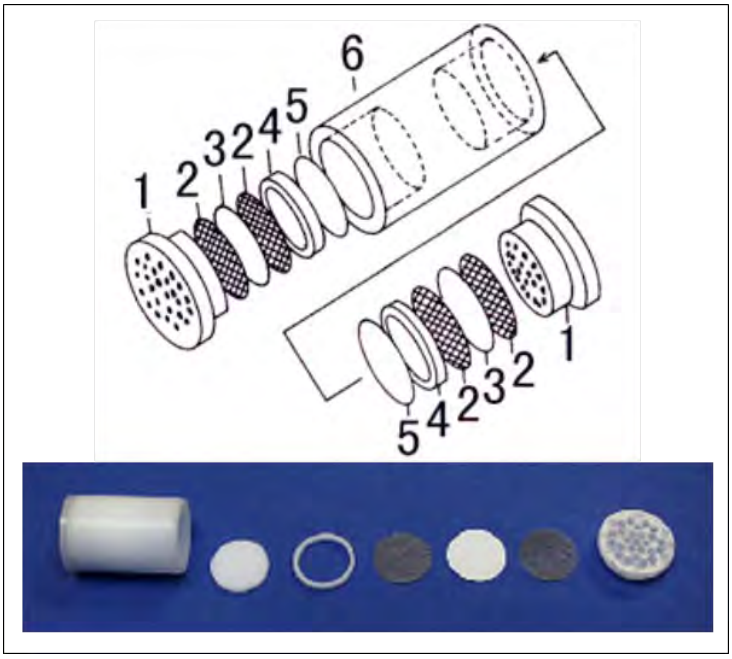


Figure 5. Assembly of Ogawa passive ammonia sampler, (1) diffuser end caps, (2) stainless screens, (3) collection pads, (4) Teflon rings, (5) Teflon disks, and (6) a sampler body **[6]**.

Two sets of field trials comparing aged and fresh training aids were completed. In the first set of trials all training aids were made from aged (1.5 years) AN-Al. Half of the aged material was placed in fresh cotton bags while the other half was left in the original 1.5-year-old bags. In the second set of trials the aged material in the old bags was compared to freshly mixed material in fresh bags. The samples tested are summarized in Table 1. All samples were tested in triplicates and compared to a blank.

Table 1. List of canine training aid types compared, including those fresh and with old wrapping and fresh and old explosive material.

Trial #	*Sample #*	*Cotton bags*		*Explosive material*	
		Fresh	*Aged*	*Fresh*	*Aged*
Trial 1	*1*	X			X
	2		X		X
Trial 2	*3*	X		X	
	4		X		X

Results – Results from the analyses of the headspace of AN-Al canine training aids, both fresh and aged, were compared. The age of the wrapping and the age of the material itself were considered. Figure 6 gives the amount of ammonia collected in the headspace from the AN component of the AN-Al material. It is clear that significantly more ammonia was collected from the headspace of the material that had been aged in the wrapping and much less ammonia was released through the new cotton bags. Figure 7 compares the amount of acid components in the headspace owing to the Al component, and, similarly, more volatiles were released from the Al through the old bags than through the new, though there was little difference between the aged and fresh material.

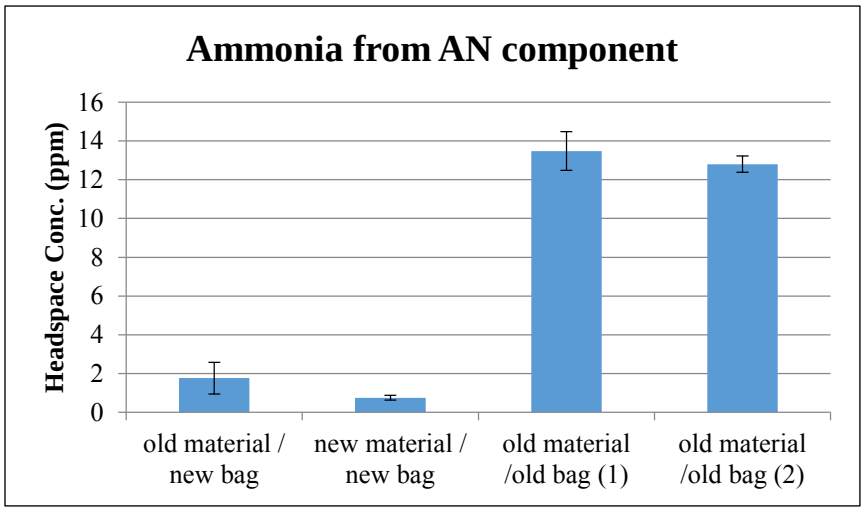


Figure 6. Amount of ammonia collected in the headspace of aged and fresh AN-Al training aids from the ammonium nitrate component.

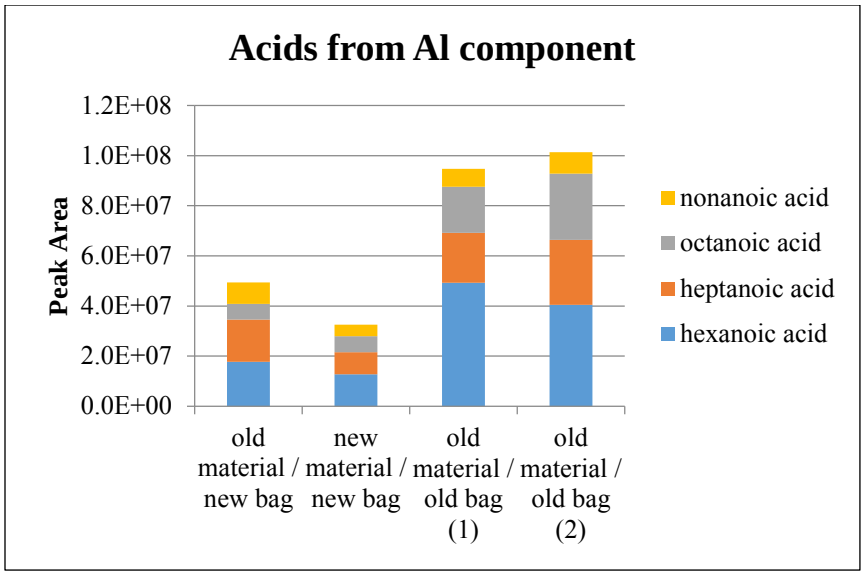


Figure 7. Acid components detected in the headspace of aged and fresh AN-Al training aids from the aluminum component.

Discussion - The results from both analyses indicate that the age of the material itself does not dictate the quantity of odor in the headspace, nor does it affect the makeup of the vapor profile. Instead the length of time the material has been in the cotton bag used for wrapping had a significant influence. It is evident that it takes time (longer than the five hour sampling time) for the odor to escape from or saturate the cotton material allowing the odorants to be detectable in the headspace.

Headspace analysis of other ammonium nitrate-based explosive material

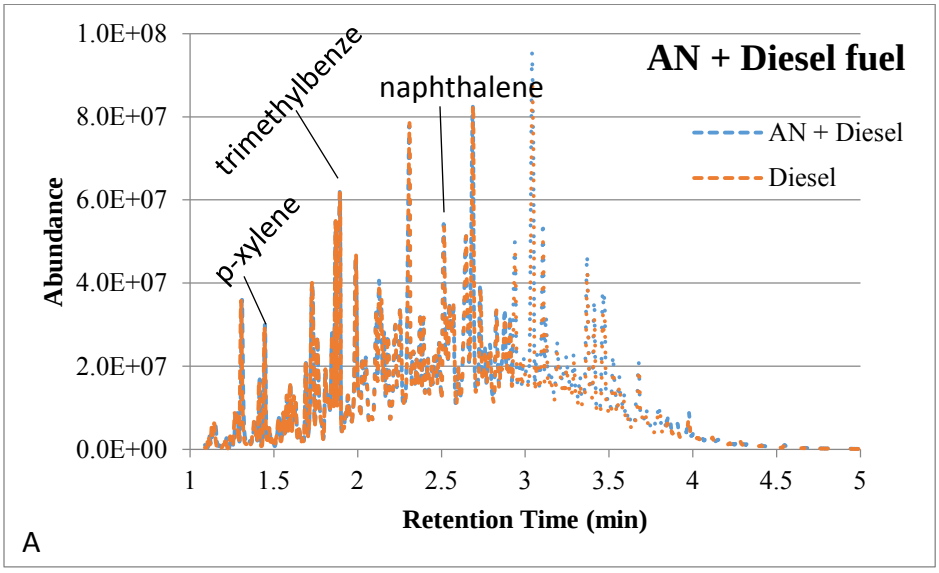
Method - The vapor signatures of AN and fuel mixtures were analyzed, comparing the mixed material to the unmixed components. Explosive mixtures included laboratory-grade AN (Sigma-Aldrich) mixed with several fuel sources purchased from local grocery and convenience stores, to include confectioners' sugar, petroleum jelly, diesel oil, and sawdust (made from scrap yellow pine). All materials were mixed in a ratio of 12:1 to equal 1.3 g of explosive material in 20 mL glass vials with septa. The samples were separately analyzed for the vapor signatures of the fuel components and for ammonia from the AN component. All sampling was repeated in triplicate and compared to blank samples.

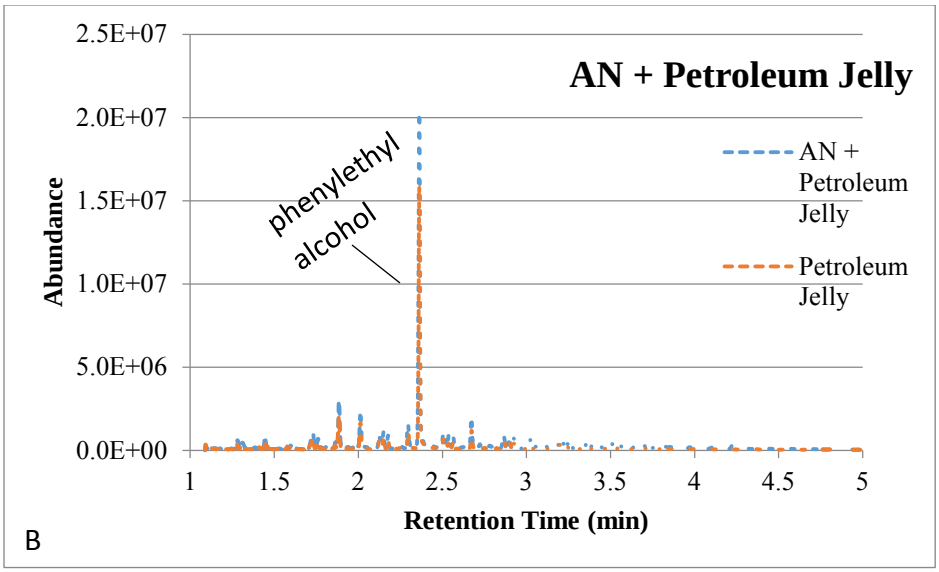
Following mixing, all sample vials were left overnight to equilibrate. On the next day, the headspace was extracted and analyzed using SPME-GC/MS, by the method described above,

with a 1 hour extraction period. The resulting chromatograms of the explosive mixtures were compared to that of the fuel components alone, prepared in an identical manner.

The ammonia in the headspace of the AN, with and without fuel, was collected and quantitated using the passive ammonia samplers, as previously described. Vials containing the explosive mixtures were placed in a sealed stainless steel chamber (600 mL in volume) containing three passive samplers for 24 hours. The samplers were then removed, and the sorbent pads were extracted and analyzed in the manner described above.

Results – The results are given as overlaid chromatograms (Figure 8). With each fuel/AN set, the same characteristic peaks from the headspace of the fuel were present and in a similar abundance indicating that the vapor signatures of the fuels were not significantly altered by physical mixing with the AN.




AN + Petroleum Jelly
Abundance
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2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
phenylethyl alcohol
AN + Petroleum Jelly
Petroleum Jelly
1
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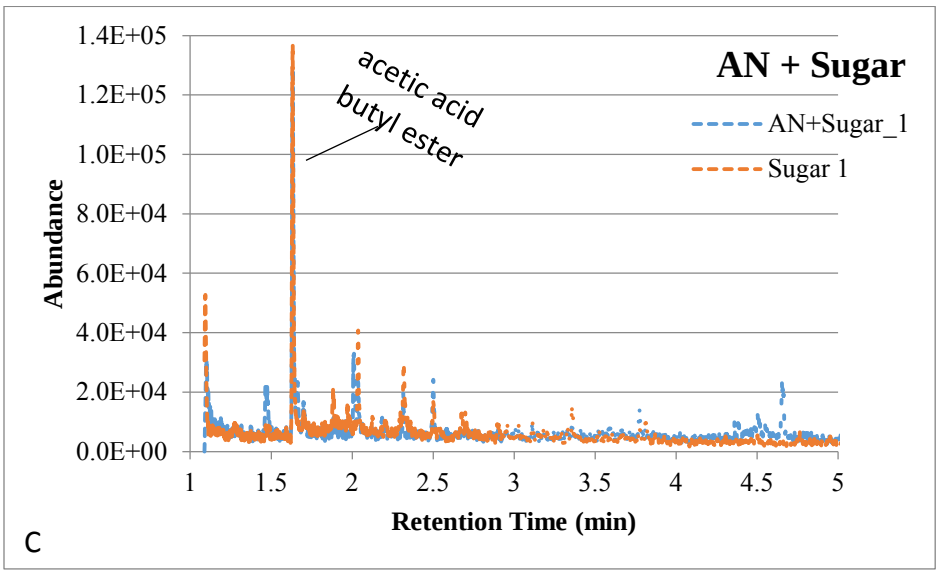
2
2.5
3
3.5
4
4.5
5
Retention Time (min)
B


AN + Sugar
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1.2E+05
1.0E+05
8.0E+04
6.0E+04
4.0E+04
2.0E+04
0.0E+00
acetic acid butyl ester
AN+Sugar_1
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2
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3
3.5
4
4.5
5
Retention Time (min)
C

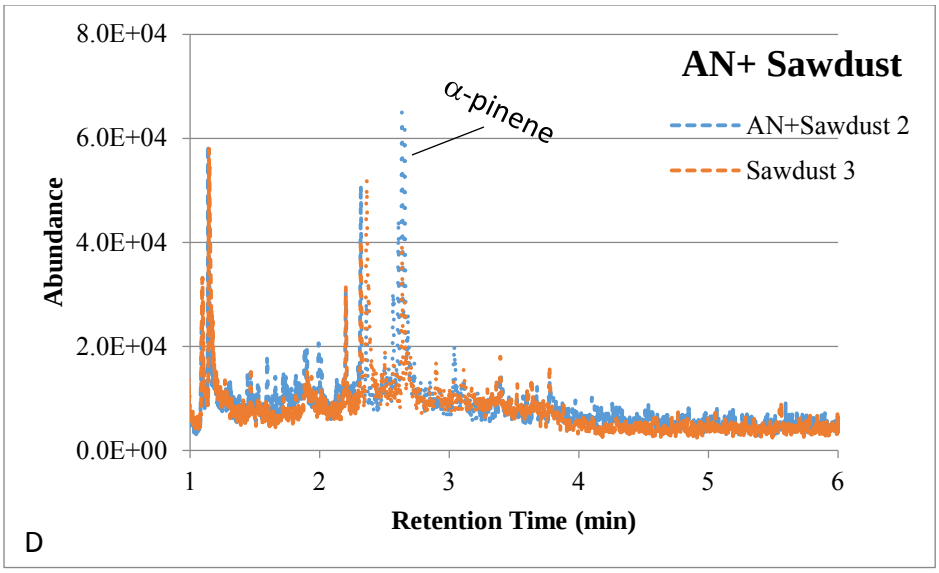

Figure 8. Chromatograms of the headspace of fuel components alone overlaid with the headspace of the fuel component mixed with AN, including A) diesel fuel, B) petroleum jelly, C) sugar, D) sawdust.

Changes in the concentration of ammonia vapor from the AN when mixed with the fuels were also measured (Figure 9). There were no statistical differences between the amount of ammonia liberated from AN mixed or alone.

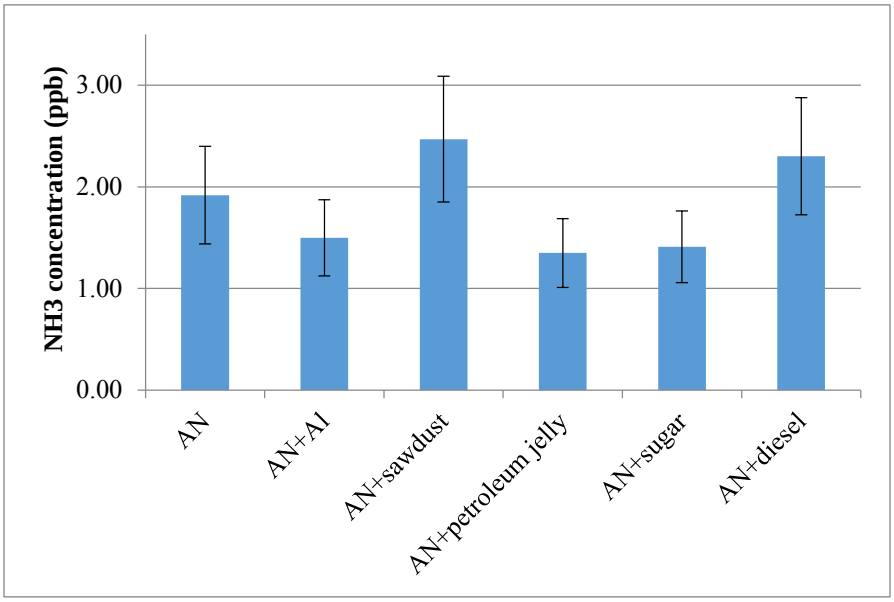

Figure 9. Headspace concentrations of ammonia above AN alone and mixed with fuel sources, to include aluminum, sawdust, petroleum jelly, sugar, and diesel fuel.

Discussion - As the purpose of the MODD or Merger is to represent mixed odor from unmixed component sources, it is imperative to determine if the physical mixing of these components

alters the presentation or make up of the odor profile. In Phase 1 of this project, the vapor signature of AN-Al, as a mixture and as individual components, was considered [5]. These results indicated that the mixing of explosive components did not significantly affect the vapor signatures of the individual components, and thus the use of unmixed material in the MODD or Merger is supported.

MODD Evaluation

Determination of appropriate cleaning procedure

Method - Several cleaning methods were evaluated with the goal of developing a reasonable protocol for cleaning the MODD in the field. Cleaning methods were evaluated by first exposing the MODD to a contaminating vapor source. For this purpose, an open vial of 1 mL of limonene, dodecane, or methyl salicylate was held in one well within the MODD for one hour. Compounds were chosen as they represent differing vapor pressures and functional groups, and are readily detected by GC/MS. The vapor source was removed and the residual vapor concentration due to adsorption to the surface of the MODD was measured. The measurement was made by placing the MODD in a 10 L Tedlar bag (SKC, inc; Eighty Four, PA), which was sealed and filled with clean air. The MODD was left in the bag for an hour allowing the contaminant to fill the headspace of the bag. The air was removed from the bag, pre-concentrated, and analyzed by GC/MS.

Preconcentration was carried out using a cooled injection system (CIS) (CIS-4, Gerstel, Inc. Linthicum, MD) online with the GC/MS. With this system, analytes in the sample headspace were drawn through a transfer line to the CIS where they were trapped on a cooled sorbent bed. After the analytes were trapped, they were rapidly desorbed to the head of the GC column by heating the CIS. In this case, the contents of the Tedlar bag were pulled at 50 mL/min towards the CIS using a heated transfer line (85 ˚C) for a total of 1L of air. Analytes were trapped onto the CIS at -10 ˚C, and then desorbed at 250 ˚C onto the GC/MS with a 60 m x 0.25 mm i.d., Rtx-1ms column (Restek Inc.). The GC column oven was held at 45 ˚C for one minute. The temperature was then increased to 250 ˚C at 40˚C/min and held for an additional 1.5 min. This measurement was compared to the results after cleaning the MODD. Upon removal from the bag, the MODD was cleaned and any remaining vapor was measured again in the same manner.

Cleaning procedures tested included cleaning in a laboratory dishwasher with detergent, scrubbing and soaking with dish soap, wiping with Clorox or alcohol wipes, or wiping with alcohol wipes followed by soaking in dish soap. Drying methods were also tested, including drying by hand following washing, and air drying overnight. All cleaning procedures were initially tested with limonene, as limonene was observed to be the most difficult to remove by cleaning. The cleaning methods that performed best at removing limonene were tested with the dodecane and methyl salicylate as well.

Results – Five cleaning procedures and two drying methods were initially tested using limonene as the contaminant. The results indicated that either wipe, Clorox or alcohol, in combination with air drying overnight, removed a majority (93% +) of the limonene from the MODD (Table 2). These two cleaning methods were evaluated on two additional contaminants with different functional groups. Results, as listed in Table 3, show that both wipe cleaning methods performed similarly with all three compounds (Figure 10). Dodecane was removed to a level below the limit of detection of the method for all trials. Approximately 5% of the limonene and 1% of the methyl salicylate was remaining with either cleaning method. All future cleaning was carried out using alcohol wipes, as opposed to the Clorox wipes as the alcohol wipes were unscented.

Table 2. Test of cleaning and drying methods using limonene as the odor contaminant, averaged amounts listed.

Cleaning Method	Drying Method	% Limonene Remaining
Dishwasher	Hand dry	44%
Dishwasher	Overnight dry	45%
Dish soap (scrub and soak)	Overnight dry	13%
Clorox wipes	Hand dry	36%
Clorox wipes	Overnight dry	5%
Clorox wipes and dish soap	Hand dry	28%
Clorox wipes and dish soap	Overnight dry	7%
Alcohol wipes	Hand dry	16%
Alcohol wipes	Overnight dry	7%

Table 3. Test of cleaning procedures with air drying overnight using three compounds as odor contaminants, carried out in triplicate.

Cleaning Method	% Remaining		
	Limonene	Dodecane	Methyl Salicylate
Alcohol wipes (1)	3.77%	-	1.85%
Alcohol wipes (2)	3.59%	-	1.10%
Alcohol wipes (3)	5.35%	-	1.67%
Clorox wipes (1)	5.53%	-	1.76%
Clorox wipes (2)	3.63%	-	0.63%
Clorox wipes (3)	8.85%	-	0.13%

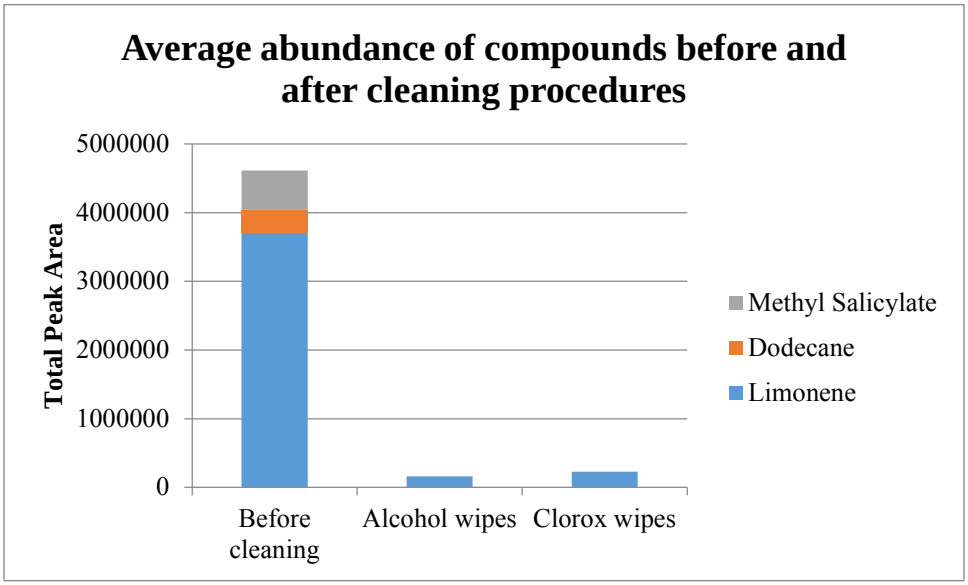

Figure 10. Average abundance of contaminant compounds from the surface of the MODD before and after cleaning with alcohol or Clorox wipes and air drying overnight.

Measurement of vapor from the MODD v. Merger

Method – For proof-of-concept, several explosive-related compounds were placed in the MODD and the Merger. The resultant vapors were measured from the outlet of each device and were compared. Analytes included 2,4-dinitrotoluene (Sigma-Aldrich), Al flake and laboratory-grade AN (Sigma-Aldrich). All analytes were placed in polypropylene, static dissipative vials, 64.93 mL or 28.71 mL (ESD Plastic Containers, Yorba Linda, CA), then placed in separate legs of the Merger or in separate wells of the MODD. Quantities of each component used in the MODD or Merger are listed in the table below (Table 4). Less quantity was used in the MODD as it was designed to require less training material than the Merger.

Table 4. Quantity of explosive-related compounds used in the Merger or MODD for vapor measurement experiments.

Compound	Mass in Merger	Mass in MODD
DNT	1 g	10 g
Al	1 g	10 g
AN	4 g in 2 vials	40 g in 2 vials

An improved method to measure DNT vapor at very low quantities was recently established at NRL. This method utilizes the CIS in line with the GC/MS, as previously done, though this method uses chemical ionization (CI) was used with MS as opposed to electron ionization (EI), allowing for greatly reduced detection limits. This CI method yielded detection limits in the low picogram range as opposed to the nanogram range of the previous method. For DNT collection the transfer line to the CIS was placed a few millimeters above either device. The CIS was chilled to 10 ˚C, and 0.825 L of air was collected at 165 mL/min. DNT was then desorbed from the CIS at 275 ˚C onto a 15 m 0.25 μm i.d., Rtx 5MS column (Restek Inc.) with a split ratio of 9:1 and a flow rate of 5 mL/min. The GC oven was started at 100 ˚C and held for 30 s, then increased to 250 ˚C at 50 ˚C/min. CI was applied in negative mode with methane as the reagent gas.

In addition to DNT, Al powder was placed in either device, and acetic acid vapor, a main vapor component of Al headspace, was collected from device outlets. The Al was left in place to equilibrate overnight (~18 hrs). 2.25 L of air was trapped from immediately above either device into the CIS-GC/MS using the previously described method for detection of organic acids above AN-Al training aids.

Finally, AN was held in the MODD or Merger for one week prior to sampling with Ogawa passive ammonia samplers. Ammonia was collected onto the sorbent pads for 48 hrs prior to analysis. Analysis and quantitation by IC was carried out in the same manner as with the AN-Al training aids.

Results – Though a greater mass of the compounds was placed in the Merger, approximately the same amount of vapor was detected from the top of each device (Table **5**). The exception was DNT collected from the top of the Merger/MODD. Approximately the same amount of DNT vapor was measured from the neck of each device, but a significantly greater amount was measured from the top of the MODD. This is likely due to the internal volume differences of the

two devices and shorter equilibration times used for the DNT analyses compared to those used for the other compounds.

Table 5. Amount (mass or concentration) of compound vapor measured from the Merger or MODD using the above described methods.

Vapor component measured	Merger	MODD
DNT (from neck) [5]	8.50 ± 0.25 ng	7.54 ± 0.80 ng
DNT (from top)	8.90 ± 3.7 pg	400 ± 22 pg
Acetic acid (from Al powder)	30.80 ± 6.38 ng	30.06 ± 8.62 ng
Ammonia (from AN)	11.70 ± 0.0731 ppb	9.67 ± 0.207 ppb

Discussion – Computational modeling demonstrated that the vapor distribution of DNT is similar in the Merger and MODD using less analyte material in the MODD [5]. Laboratory results have confirmed this to be true for several analytes, though results from DNT vapor collection at the top of the devices suggests that the similarity may be time dependent. Overall, the MODD was shown to efficiently distribute vapor from small quantities of several explosive components.

Mixing of odorants

Method – The relationship of mixed vapors in the MODD/Merger was further explored by varying compound ratios and equilibration times. Additionally, compounds with different functionalities and volatilities were evaluated in the MODD. Similarities or dissimilarities between devices, equilibration times, and compound ratios are demonstrated by comparison of vapor profiles. In this work the vapor profile was expressed in terms of the ratio of vapor quantities (by mass) collected from the headspace, as opposed to total vapor collected.

For all experiments, aliquots of neat methylsalicylate (MeS), limonene (Lim), or decane (Dec) (Sigma-Aldrich) were put into 28.71 mL, static-dissipative vials (ESD Plastic Containers) which were placed into the MODD or Merger for a given equilibration time. Vapor samples were then taken from immediately above the gratings of the devices. No restrictor plug was used in the MODD. For comparison purposes, the compounds were also placed into a 600 mL, Sulfinert-coated, stainless steel, headspace sample chamber, previously designed at the Naval Research Laboratory [7]. All vapor samples were collected through the heated transfer line at 75

mL/min and onto a coated baffle liner (Gerstel Inc.) held at -20 ˚C in the CIS. Analytes were desorbed from the CIS liner at 250 ˚C, and injected onto a 60 m x 0.25 mm i.d. Rtx-1ms (Restek) GC column at 4 mL/min in an Agilent 7890A GC. The GC column oven was initially heated to 45 ˚C for one minute. The temperature was then increased to 250 ˚C at 40 ˚C/min and held for an additional 1.5 min. The MS was a JEOL AccuTOF GCv (JEOL USA, Inc., Waterford, VA). Vapor volumes collected from the Merger/MODD and sampling chamber totaled 750 mL and 100 mL, respectively. The mass of the analyte in the collected vapor was determined by comparison to external calibration curves. The ratios of the measured masses were then compared to calculated ratios based on reported vapor pressures of the compounds.

The first set of experiments compared the Merger and MODD. MeS and Lim were placed separately in either device, and the equilibration times and the amounts of each compound were varied according to Table 6. In a second set of experiments pairs of compounds of varying vapor pressures and functionalities were placed in MODD. For comparison, the same compounds were also sampled from the headspace sampling chamber after four hours equilibration. This comparison was used to confirm that ratios of odorants in the headspace remained the same in alternate sampling scenarios as those at the MODD outlet.

Table 6. Equilibration time and amounts of MeS and Lim in the Merger/MODD.

1 hr	2 hrs	23 hrs
1 mL MeS / 1 mL Lim	1 mL MeS / 1 mL Lim	1 mL MeS / 1 mL Lim
1 mL MeS / 2 mL Lim	1 mL MeS / 2 mL Lim	1 mL MeS / 2 mL Lim
2 mL MeS / 1 mL Lim	2 mL MeS / 1 mL Lim	2 mL MeS / 1 mL Lim

Results - When comparing MeS and Lim in the Merger (Figure 11), vapor ratios were statistically similar within each quantity set used, indicating that a equilibration time of less than1 hour was adequate for these compounds to reach equilibrium. Increasing the amount of the Lim, the higher volatility compound, yielded an increase in the presence of Lim vapor compared to MeS, while increasing the amount of MeS had little effect on this ratio. This effect was expected, and should also hold true in the field, as the amount of MeS vapor detected was limited by its lower equilibrium vapor pressure, while Lim, having a substantially higher equilibrium vapor pressure, was limited by its rate of evaporation. In other words, the MeS reached a point where it was at its equilibrium partial pressure, thus adding more MeS did not

increase its concentration. Lim, with a higher vapor pressure, on the other hand, did not reach equilibrium as quickly.

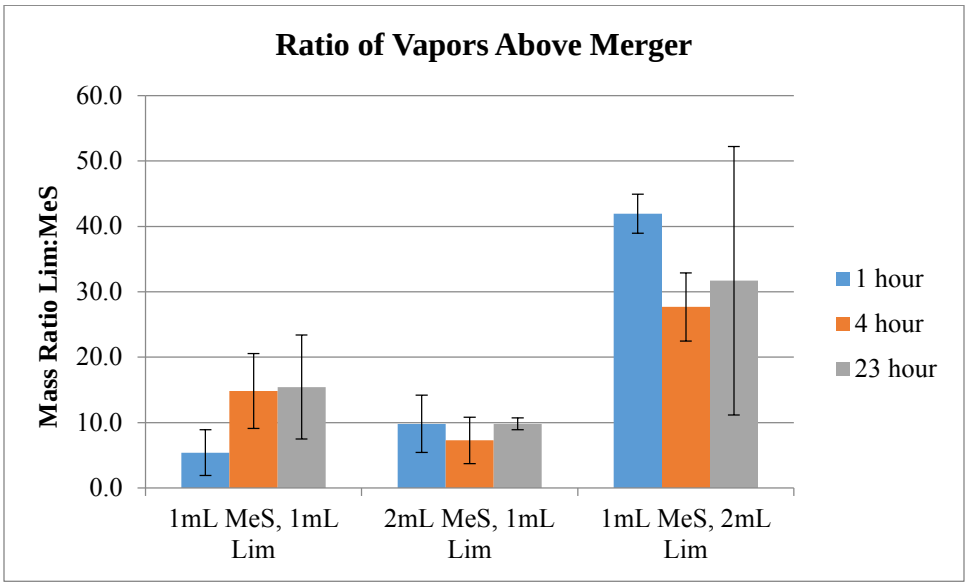

Figure 11. Averaged ratios of Lim to MeS detected from top of Merger by CIS-GC/MS following 1 hr, 4 hrs, and 23 hrs equilibration times.

Results from the MODD (Figure 12) agree with observations from Phase 1, indicating that the MODD favors the higher volatility compound compared to the Merger, as can be seen from the higher Lim to MeS ratios across all samples. There was no significant difference between different equilibration times, though 1 hr seems to be consistently higher than the other times. This might indicate that the compounds do not come to equilibrium in the MODD as quickly as they do in the Merger. It would thus be recommended to increase the equilibration time to at least an hour prior to presenting the device to the canine. Varying ratios of the compounds in the MODD yielded similar results to the Merger.

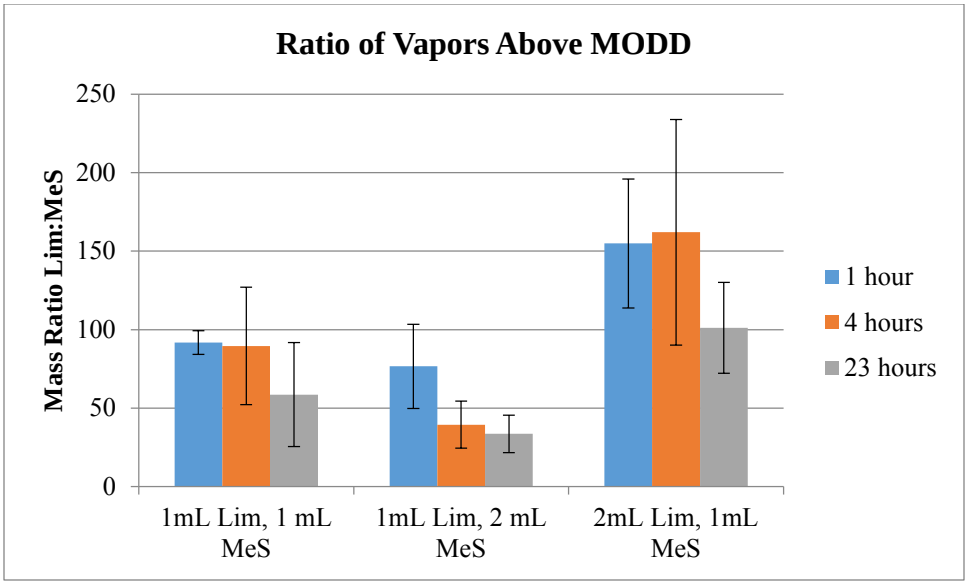

Figure 12. Averaged ratios of Lim to MeS detected from top of MODD by CIS-GC/MS following 1 hr, 4 hrs, and 23 hrs equilibration times.

In the second set of experiments, pairs of compounds of varying vapor pressures and functionalities were placed in the MODD or sampling chamber, and the vapors were measured after 1, 4 or 23 hours. The resulting ratios of Lim to Dec (Figure 13) and Lim to MeS (Figure 14) in the MODD as well as in the chamber were statistically similar to one another and to the predicted value indicating no alteration of the odor profiles from the MODD outlet, and no differences in interactions between the compounds and the PVC material.

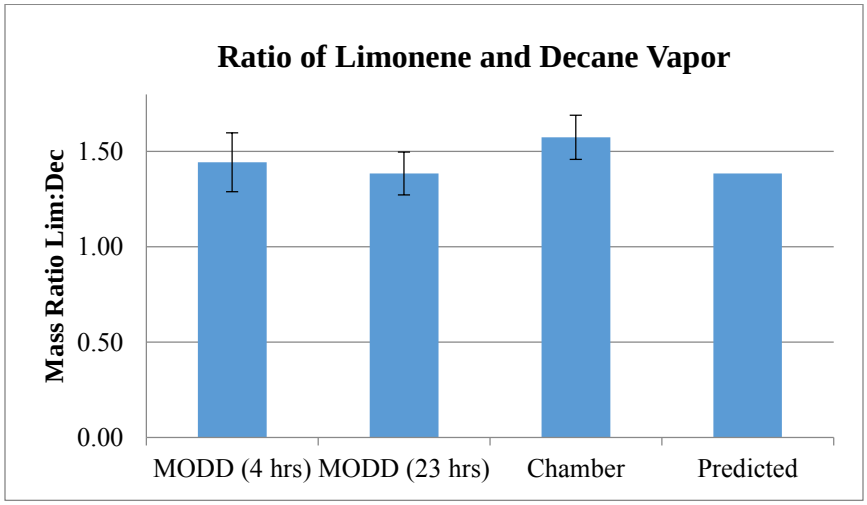

Figure 13. Averaged ratios of Lim to Dec detected from top of MODD following 4 hrs, and 23 hrs equilibration times, and compared to that from the headspace sampling chamber and to the predicted value.

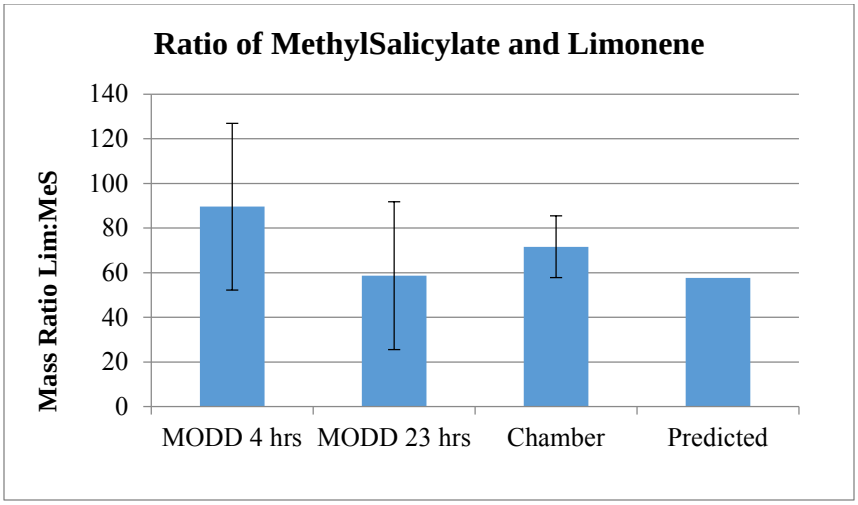

Figure 14. Averaged ratios of Lim to MeS detected from top of MODD following 4 hrs, and 23 hrs equilibration times, and compared to that from the headspace sampling chamber and to the predicted value.

Discussion - In Phase 1, experiments were carried out to assess the mixing of multiple vaporous components in the MODD and Merger. Methylsalicylate and limonene were evaluated in individual devices comparing the resulting vapor from a mixture of the two compounds and as separated components. Phase 2 continued this line of experiments, focusing on other variables affecting the vapor ratio output. Results showed similarity in the vapor distribution between the Merger and MODD as quantities of compounds are altered, though the large volume of the Merger tended favor the lower volatility compound. When vapor ratios were compared to the headspace from an alternate container or to calculated values, the vapor profiles were statistically the same to that in the MODD. The MODD thus accurately portrays the mixed odor of these separated compounds at varying equilibration times and compound quantities.

HMEs in MODD

Method - The odors from fuels (~1 g) often used in HMEs were assessed from the outlet of the MODD, and compared to that from open vials. Fuels were also placed within the MODD along with separate vials of 2 g of laboratory-grade AN or PC (Sigma-Aldrich). The headspace of the fuel was collected using SPME, as discussed previously, exposed directly over the MODD and extracted overnight. In all experiments, the MODD was used with no restrictor plug. As the abundance over the open vial was much greater, shorter extraction times of two hours were used.

Analytes on the SPME fiber were thermally desorbed in the GC/MS inlet using the same method previously used for HME vapor profile determination. Normalized values of the main headspace components were plotted and compared.

Results – As to be expected, there were many components present the headspace of diesel fuel, including toluene, *p*-xylene, trimethylbenzene, and naphthalene. All of these components could be detected from the vial, above the MODD, and above the MODD also containing PC and/or AN. Slight variations in relative amounts of the headspace components were noted between fuel above the vial vs. above the MODD (Figure 15). This is likely due to the shortened SPME extraction for the vial sample. There was little variation between the relative amounts of headspace components in the MODD with and without the oxidizers.

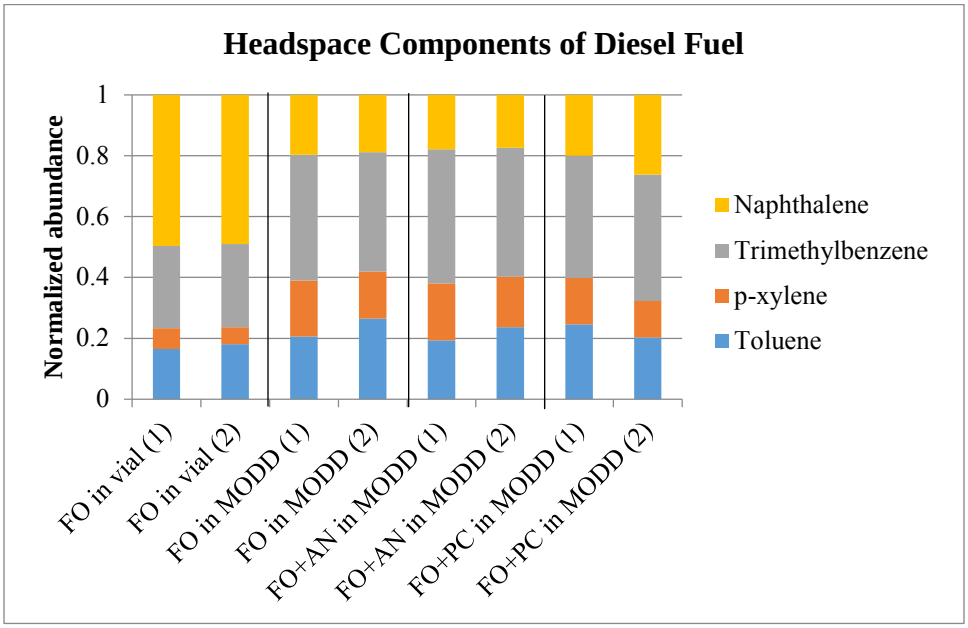

Figure 15. Normalized abundance of major headspace components of diesel fuel in a vial and from the MODD.

The main components detected from the headspace of the sawdust sample were nonanal, 2-ethyl-1-hexanol, and α-pinene (Figure 16). All three components were detected from every sample with similar relative values indicating no change in the odor profile in the MODD or in the presence of PC.

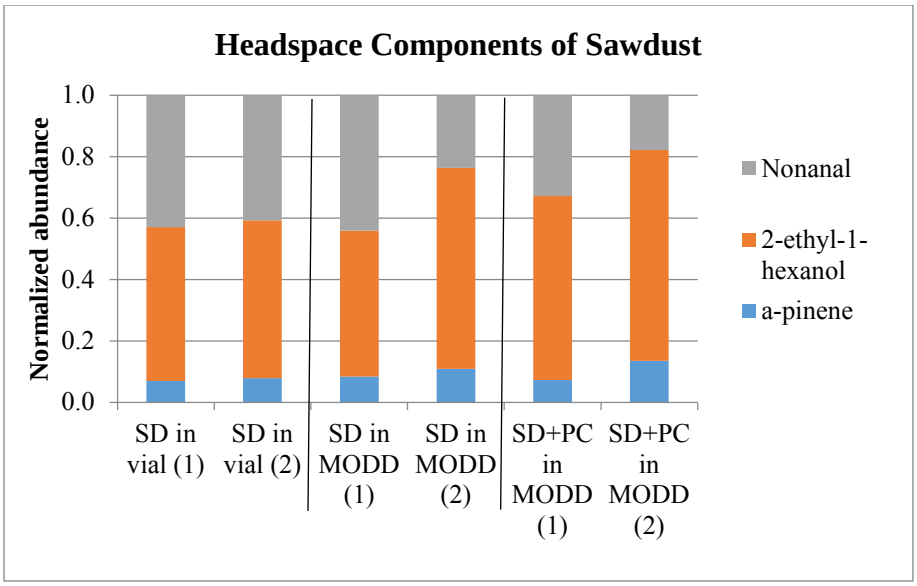

Figure 16. Normalized abundance of major headspace components of sawdust in a vial and from the MODD.

Phenylethyl alcohol was the main headspace component in petroleum jelly (Figure 17), and could be detected from both above the vial and the MODD. Few other components could be detected from above the vials, and no others could be detected from above the MODD. However, it was noted that the total abundance of the phenylethyl alcohol in the MODD with and without PC was similar (Figure 17).

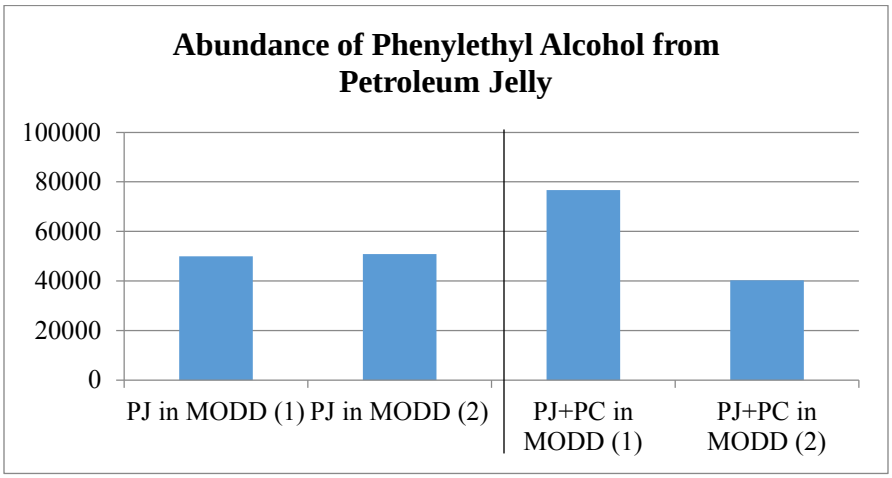

Figure 17. Total abundance of phenyethyl alcohol from petroleum jelly placed in MODD.

Discussion – When using the MODD for canine training it is imperative that the canines are trained on odors indicative of the actual mixed explosive. Previously, in this report, it was shown that the physical mixing of HME components did not change the odor of the individual

components. It has now also been shown that holding the components in the MODD does not alter the odor profile. Overall this implies that the separated components in the MODD will portray an accurate mixed odor for canine training.

Preliminary Canine Trials, Modifications to MODD Design, and Additional Testing

Preliminary canine trials – Set 1

Method - Preliminary canine trials were carried out with three canines, previously trained to AN only. Two compounds of a higher and a lower volatility were tested to ensure that the final design functions for a variety of target odors. Smokeless powder (SP) and AN, provided by the canine handlers, were used as target odors. Smokeless powder (higher volatility) was considered an easier target for the canines, while AN (lower volatility) was more difficult. All testing was carried out in an open, unoccupied hallway, and all lineups consisted of four blank MODDs (i.e. containing no odor) and one MODD containing the target. The order was changed at random between each run, and the handler was blinded to the type and location of the target odor during all runs.

Initial testing runs were carried out to confirm that each canines was proficient in detecting AN as well as SP. Glass jars containing either material were placed in separate line-ups of six scent boxes. The scent boxes were purchased commercially and were regularly used for training.

The next phase of testing was carried out for the purpose of acclimating the canines to the MODD. A smaller amount of SP was placed directly under the grating the MODD. The SP was placed in this manner to "teach" the canine to sniff at the outlet of the MODD. Further MODD testing was not carried out until all canines were acclimated to the MODD as determined by a correct positive response to the MODD containing the target.

In the final phase of testing, the canines were directed to locate targets within the lower portion of the MODD. Initially, one vial (PFA; Savillex, Eden Prairie, MN) of SP was placed in the MODD without the restrictor plug. After a minimum equilibration or "sit" time of 1.5 hours, the canines were directed to search lineups containing five MODDs, one containing the target. This was repeated with AN and a similar sit time.

Results – All three canines correctly located the explosive material in the initial runs with no false alerts, indicating sufficient proficiency on the odor in question. When SP was placed under the grating of the MODD, all canines, again, alerted to the correct MODD on the first try with no false alerts.

During the final trials no canine alerted or showed a change in behavior to the correct device in any run. As the canines did not successfully locate the MODD containing either explosive material, the amount of smokeless powder was increased using 4 vials of SP in the MODD with a soak time of less than one hour. One of three canines alerted to the correct device. The other two canines did not alert or show a change in behavior.

Discussion - It was concluded from these trials that there was an insufficient amount of odor present at the top of the MODD for detection using the allotted "sit" times. It was hypothesized that increasing the sit time substantially would allow for detection though this is impractical for actual training scenarios. To increase the odor available at the outlet without increasing sit time, the MODD was redesigned with a wider neck lined with a Teflon insert.

MODD modification – Widen neck

To allow a greater odor concentration to reach the outlet of the MODD and to reduce sit times, the neck of the MODD was widened. Computational modelling, as used in Phase 1, was utilized for examining the vapor distribution of a single component in each design. The vapor distribution at the top of the original MODD implied a symmetric distribution for a single component in the MODD, meaning multiple components in the MODD would mix thoroughly and the canine would not be able to distinguish the individual component vapors [5]. This was repeated with two possible redesigns (Figure 18). The first design simply increased the opening of the neck to its maximum width. With this design the length of the neck had to be shortened. The model of this design indicated an asymmetric odor profile at the outlet (Figure 19). A Teflon insert was then added to encourage a symmetric odor plume, and it also promoted vapor mixing while reducing adsorption in the neck area. The model of the vapor distribution of this design at the outlet indicated symmetric mixing (Figure 20). This design was thus used for further testing.

Figure 18. Images of the MODD with various modifications of the neck. Top: no modification; bottom, left: neck widened; bottom, right: neck widened and Teflon insert added.

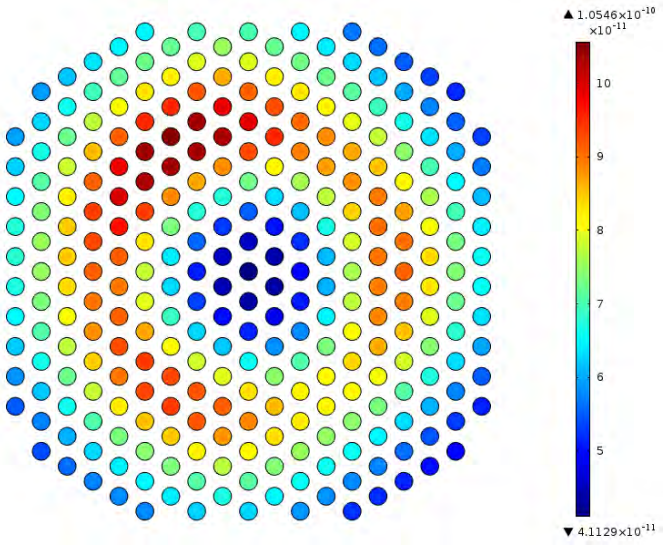

Figure 19. Model of the vapor distribution at the MODD outlet from a single vapor source in the MODD, neck widened, no insert.

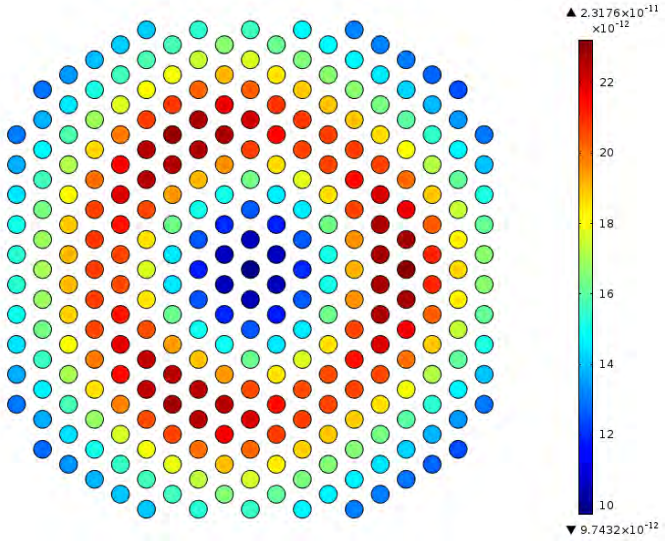

Figure 20. Model of the vapor distribution at the MODD outlet from a single vapor source in the MODD, neck widened with Teflon insert.

Experiments, discussed below, were conducted to compare the MODD-1 (the original MODD) and MODD-2 (wider neck) (Figure 21). Images include restrictor plugs, though restrictor plugs were removed for testing. The vapor released from surrogate mixtures, as well as HME compounds, were measured at the outlets of both the MODD-1 and MODD-2.

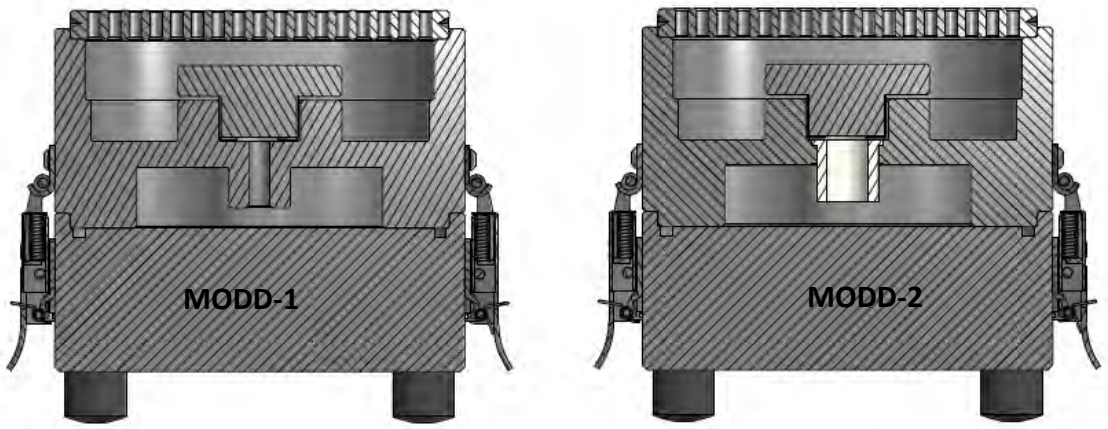

Figure 21. Schematics of the MODD before (MODD-1) and after (MODD-2) widening the neck.

Method – The first set of tests analytically evaluated the symmetry of the vapor output of the MODD-1 and MODD-2. This was carried out by placing separate vials of 1 mL of MeS and 1 mL of Lim in opposite wells in the MODDs. Two SPME fibers were then placed over the MODDs, in line with each vial, with the assumption that if the plume was perfectly symmetric then the ratio of MeS to Lim would be the same at each fiber. This experiment was carried out

with equilibration times of 2 and 4 hours, and the analysis was performed using the previously established methods.

For comparison to experiments previously run with the MODD-1, Lim and MeS were again placed separately in the MODD-2 and the ratio of the masses collected were compared. For additional comparisons of the MODD-1 and -2, separate experiments with HME fuels (Al powder, sawdust, and diesel fuel) and DNT were carried out, again mirroring those previously conducted with the MODD-1.

Results – Results of the symmetry experiment yielded no statistical differences between the MODD-1 and MODD-2 (Figure 22). The ratio of Lim to MeS at the position of Fiber 1 was consistently higher than at the position of Fiber 2, but the difference was also not statistically significant, meaning there was little asymmetry at the MODD outlets.

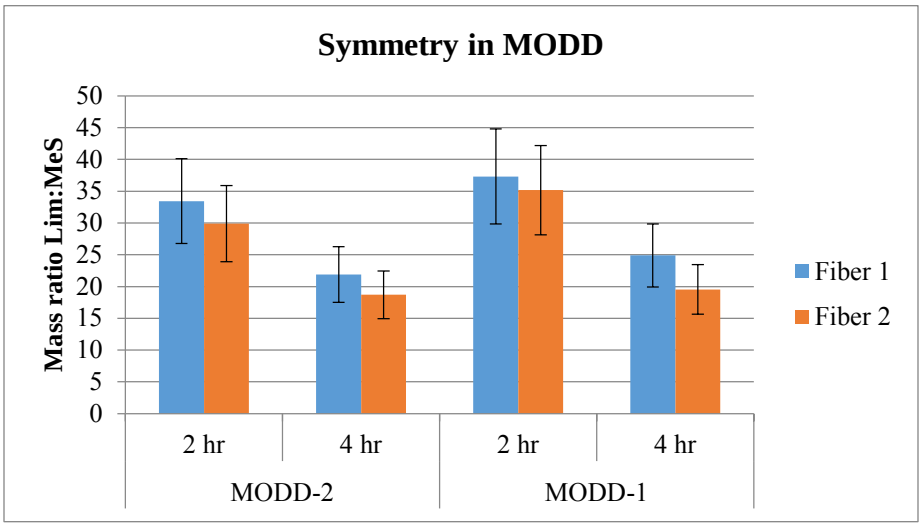

Figure 22. Figure compares the ratio of analyte masses (Lim:MeS) collected from above the MODD-1 and MODD-2 in two positions, labeled Fiber 1 and Fiber 2.

MeS and Lim were also measured in the MODD-2 using the CIS-GC/MS for comparison to previous measurements taken with the MODD-1. Results indicated that the ratios collected from both MODDs were statistically similar (Figure 23). Additionally, it was estimated that the actual quantities of Lim and MeS collected was about five times higher in the MODD-2 than those measured from the MODD-1.

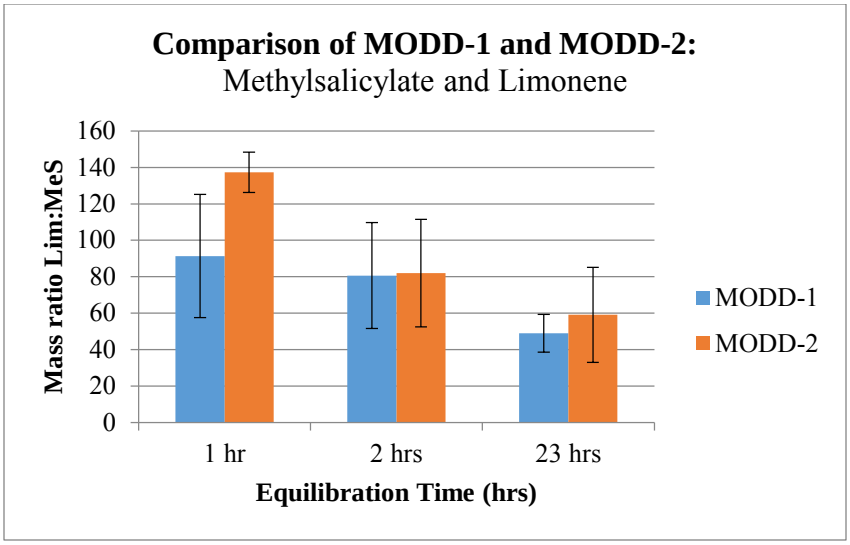

Figure 23. Averaged mass ratios of Lim to MeS detected from the MODD-1 and MODD-2 outlets following 1, 4, and 23 hrs of equilibration.

Vapors from HME fuels, including diesel fuel, sawdust, and Al powder, and DNT were assessed from the outlet as well. Quantities of acetic acid (from Al powder) and DNT vapor from above the MODD-1 and MODD-2 were compared. The amount of acetic acid collected from the MODD-2 was approximately three times greater than that of the MODD-1 (Figure 24), and approximately five times more DNT was collected (Figure 25). Normalized values of the main headspace components of sawdust (Figure 26) and diesel fuel (Figure 27) were compared, and no difference in odor profiles between the MODD-1 and -2 were observed.

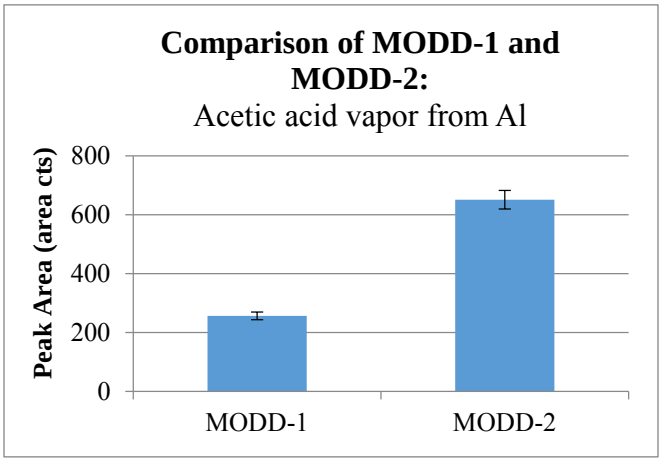

Figure 24. Measurement of acetic acid vapor collected from above the MODD-1 and MODD-2.

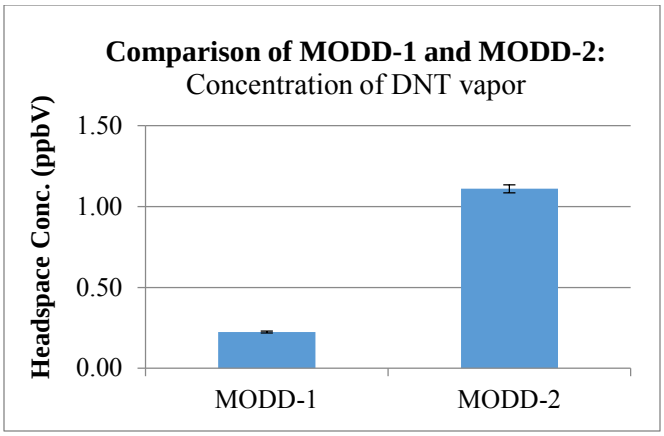

Figure 25. Measurement of DNT vapor collected from above the MODD-1 and MODD-2.

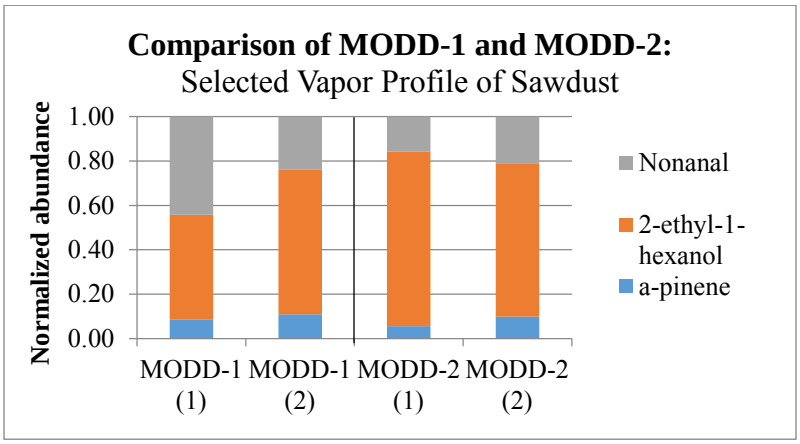

Figure 26. Normalized abundance of the main headspace components of sawdust in MODD-1 and MODD-2.

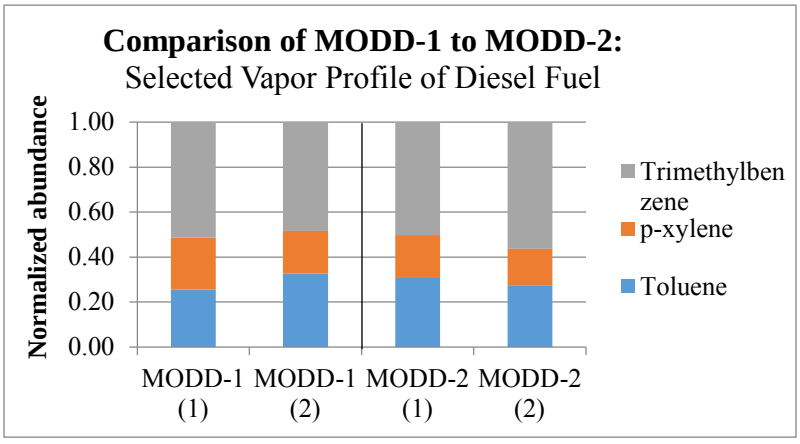

Figure 27. Normalized abundance of the main headspace components of diesel fuel in MODD-1 and MODD-2.

Discussion – Comparisons between the MODD-1 and MODD-2 reveal an increase in the amount of analyte present at the outlet of the MODD-2 as intended. The design change did not affect the

actual vapor profiles, however, thus canines should recognize the odors from separated components in either the MODD-1 or -2 as mixed. Additionally, design changes did not reduce the symmetry of the vapor distribution in the MODD-2, accordingly, the new design still promotes complete mixing of separated components as in the previous design.

Preliminary canine trials – Set 2

Method – A subsequent set of preliminary canine trials was carried out with additional trained canines. The responses of these canines to the modifications of the MODD were compared with the goal of a finalizing a design suitable to the canine's odor detection limit without requiring a long sit time.

Two compounds of a higher and a lower volatility were again chosen. Smokeless powder was used as the higher volatility target, while potassium chlorate (PC) was considered the lower volatility component. All targets were provided by the canine handlers. Testing was carried out in an unoccupied room containing two rows of bunk beds and lockers along either wall with a hall down the middle. MODD testing was carried out in lineups down the middle area. As was done in the first set of trials, all lineups consisted of one MODD containing the target and four blank MODDs, the order was changed between each run, and the handler was blinded to the type and location of the target odor during all runs.

Initial runs testing the canine on the target odors without using the MODD were carried out first. Bags containing SP or PC were hidden amongst the beds/lockers. The canines were directed to search the entire area and to indicate to the handler where the target was located. The handler communicated the canine's final response to the assessor.

Again, an acclimation phase was conducted in the same manner as previously carried out with a small amount of SP placed immediately under the grating of the MODD. Further MODD testing was not completed until all canines were acclimated to the MODD as determined by a correct positive response to the MODD.

All further runs tested variations of the MODD design, and were conducted using three vials of either target material each. Two versions of the MODD (MODD-1 and MODD-2) were compared. The MODDs were also used with and without the grating and with and without a restrictor plug over the opening of the neck.

Results - Results are summarized in the table below (**Table 7**). All participating canines easily detected SP and PC in the initial runs (runs #1 and 2), and SP in the acclimation run (run #3). Following these runs, the canines were then asked to check cleaned MODD parts, i.e. top and bottom separated. These MODDs had previously contained SP, PC, AN, or DNT, but had been cleaned according to the previously determined protocol. None of the canines showed interest in any MODD part (run #4), proving the cleaning process was sufficient.

The MODD tests began using smokeless powder, the easier target, in the MODD-2 with the grating and without the plug, and following a 1.5 hour sit time (run #5). No canine showed interest or responded to this set up. MODD-1 was not tested with this set up as the MODD-1 delivers a lower concentration of odor at the outlet than the MODD-2, and thus would not likely have yielded a positive response.

The grating was then removed from the MODD-2. Without the grating or plug, all canines alerted to the smokeless powder after a sit time of only about 15 minutes (run #6). Using the same parameters, SP in the MODD 1 was also detected (run #7). When PC was set up in the same manner in the MODD 1 two out of three canines positive gave responses (run #8).

With successful detection of both SP and PC with MODD-1 and -2 without the grating or restrictor plug, the plug was incorporated into the scenario, starting with MODD 1 containing SP (run #9). No canine responded to this set up, though one did show interest but failed to give a final response. With SP in the MODD-2 with the plug, however, all canines gave a positive response (run #10). Repeating the same set up with PC, one of two canines detected the target (run #11). When the sit time was extended to 30 minutes both canines were able to locate the PC (run #12).

Table 7. Results from preliminary set of canine trials used to evaluate variations of the MODD.

Run #	Type of run	Compound	MODD 1 or 2	MODD grating	MODD plug	Soak time	Number of pos. responses
1	Initial run	SP	n/a	n/a	n/a	20 min	3/3
2	Initial run	PC	n/a	n/a	n/a	20 min	3/3
3	Acclimation to MODD	SP	MODD 2	yes	n/a	5 min	3/3
4	Blanks	n/a	MODD 1 and 2	n/a	n/a	n/a	0/3
5	MODD testing	SP	MODD 2	yes	no	1.5 hr	0/3
6	MODD testing	SP	MODD 2	no	no	15 min	3/3
7	MODD testing	SP	MODD 1	no	no	15 min	3/3
8	MODD testing	PC	MODD 1	no	no	15 min	2/3
9	MODD testing	SP	MODD 1	no	yes	15 min	0/2 (1 interest)
10	MODD testing	SP	MODD 2	no	yes	15 min	2/2
11	MODD testing	PC	MODD 2	no	yes	15 min	1/2
12	MODD testing	PC	MODD 2	no	yes	30 min	2/2

Discussion - The canines responded positively to the MODD design itself. No issues were encountered teaching the canines to sniff from the top of the MODD, with no canine requiring more than two passes by the MODD to be proficient.

It was evident that the MODD grating prevented detection of the target odor, though it was unclear if this was due to a detection limit issue, or if the reservoirs of available odor were insufficient; i.e. the initial sniff consumed the entire volume. It was clear that the smaller neck of the MODD-1 does make sampling more difficult for the canines as does the restrictor plug. For future applications the restrictor plugs could be used to lower odor availability during training and threshold testing.

MODD modification – Remove/change grating

Based on the results from the first set of preliminary canine trials, the neck of the MODD was widened (MODD-2). Following the second set of trials, the MODD-1 design was eliminated, focusing on the MODD-2. Additionally, two variations of this design, the MODD-2, (now referred to as the MODD) were evaluated. The first variation included a modified grating. The grating was thinned, potentially reducing restriction due to absorption of analyte vapor to the PVC as it passes through the grating holes, thus allowing more vapor to reach the canine nose. This version was tested without the restrictor plug. In the second variation, the grating was

removed altogether, though the restrictor plug was utilized. Subsequent laboratory evaluations on these variations investigated the amount of odor entering the surrounding environment from the MODD, both passively and actively by canine sniff, and effect of the MODD design on the odor concentration at different points in and around the MODD.

Method – Vapor diffusion into the environment was measured by placing the MODD containing a target analyte into a Tedlar bag. The Tedlar bag was filled with air, and the MODD was sealed in the bag allowing the vapor to diffuse into the bag. Methyl salicylate (1 mL) was placed into a single well in the MODD. The MODD was then placed into a 25 L Tedlar bag (Restek Inc.), which was then sealed and evacuated. The bag was filled with 15 L of dry house air. The bag was oriented in such a way that the MODD sat evenly across the bottom seam with the air sampled at the top, as far from the MODD as possible. Following a four hour soak time in the bag, 1.5 L of this air was collected at 75 mL/min, then trapped and analyzed by CIS-GC/MS using the same method parameters as previously used for MeS analysis. MeS collected from the bag was quantified by comparison to an external calibration curve and the quantities were compared for the various configurations of the MODD, run in triplicate.

To eliminate concern that the canine depletes the vapor held in the MODD on the first sniff, leaving an insufficient amount of analyte for detection, an experiment was designed to mimic a dog sniff over the MODD. With a target analyte held within the MODD, consecutive collections were made using 1 L VeriAir Flex manual inflating sample bags (Environmental Monitoring Systems; Charleston, SC) that can collect one liter of air in several seconds. One mL of methyl salicylate was placed into a single location in the MODD, and was allowed to equilibrate for 1 hour. The manual-fill bag was attached to a piece of tubing with a 2" diameter funnel at the other end. The funnel was placed several centimeters above the grating or plug, and the bag was rapidly filled. This was quickly repeated two additional times, with the total sampling time being less than one minute. Air was collected from each bag and analyzed by CIS-GC/MS using the previously described method. All measurements were taken in triplicate and compared to an external calibration curve for quantification.

Vapor pooling in the upper chamber of the MODD was measured with each MODD variation. To do this a method for quantitation with SPME-GC/MS using an externally sampled internal standard (ESIS) was developed to estimate vapor concentration. One mL of methyl salicylate was again placed into a single location in the MODD. The vapor was allowed to

equilibrate for both 30 minutes and 4 hours. Following the equilibration time, a SPME fiber was placed in a position in or above the MODD. Vapor was extracted with the fiber for two hours. The ESIS, methyl benzoate (20 ppmV in water), was applied to the fiber by immediately placing the fiber into the headspace of a 4 mL vial containing the internal standard, for two minutes. Analysis was carried out by GC/MS with thermal desorption, as used for the symmetry experiment, and quantitation was carried out by comparison to a calibration curve created using SPME with the same extraction time over solutions of MeS diluted in water to varying concentrations. SPME positions included: (1) in the neck of the MODD (with grating) or immediately next to the plug (without grating), (2) at the height of the grating, or (3) 5 cm above the height of the grating, as shown in Figure 28.

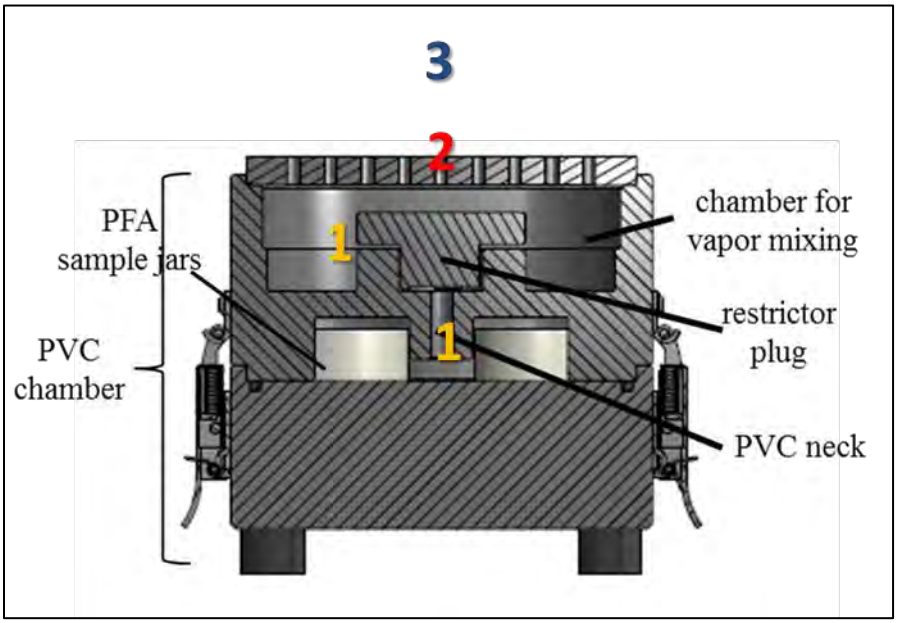

Figure 28. Diagram depicting the positions for SPME sampling over/around the MODD.

Results – The release of vaporous components into the headspace around the MODD, as measured from within the Tedlar bags (MODD-2) was evaluated and compared for the four design variations. These included the MODD with no grating and no restrictor plug (baseline), no grating with a plug, original grating with no plug, and thinned grating with no plug (Figure 29). Results suggested that the grating does function to reduce vapor entering the environment. There was a 50% reduction of MeS measured from above either grating compared to above the restrictor plug, and about an 80% reduction compared to the baseline with no restrictor plug or grating. The use of the thinned grating compared to the original does not appear to permit additional vapor to enter the headspace.

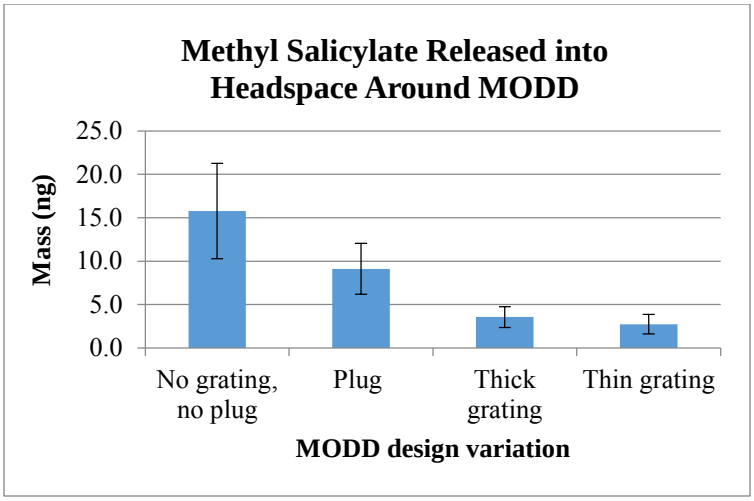

Figure 29. Mass of methyl salicylate vapor collected from the headspace surrounding the MODD.

Sequential mock dog sniffs were taken from above the MODD. Results, given in Figure 30, reveal no significant difference between the mass of MeS collected from each subsequent "sniff". There was also minimal variation between the amounts collected from each version of the MODD. The results do not support the hypothesis that canines deplete the odor held under the grating in the MODD.

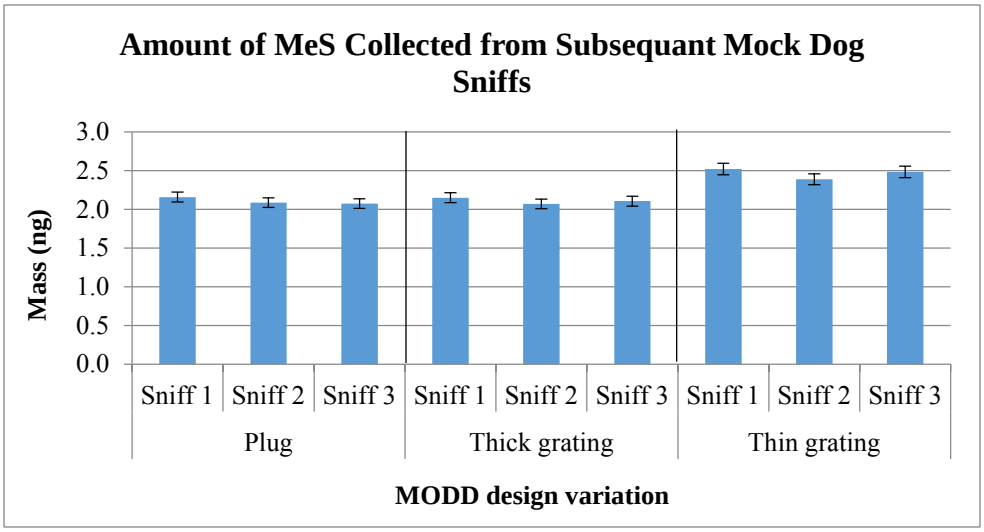

Figure 30. Mass of MeS collected from three subsequent mock dog sniffs above the MODD.

SPME was used to measure the quantity of analyte vapor from specific locations in and around the MODD. Again, results are given for the MODD with and without the restrictor plug or grating. Equilibration times of 30 min and 4 hours were compared, and results showed little difference between the amounts of compound detected indicating that 30 minutes is an adequate equilibration time for this compound in the MODD (Figure 31). Comparing MODDs with the

thick and thin grating, there was no significant difference at any position. The plug, however, did act to impede the release of a significant amount of MeS vapor, as can be seen from the large difference between the amounts of compound detected in the neck vs. next to plug at neck height. During an actual dog sniff, the canine nose is close to the plug or slightly above the grating, depending upon the MODD configuration. Comparing these positions, the canine receives about twice as much odor from the MODD with the plug then the MODD with either grating.

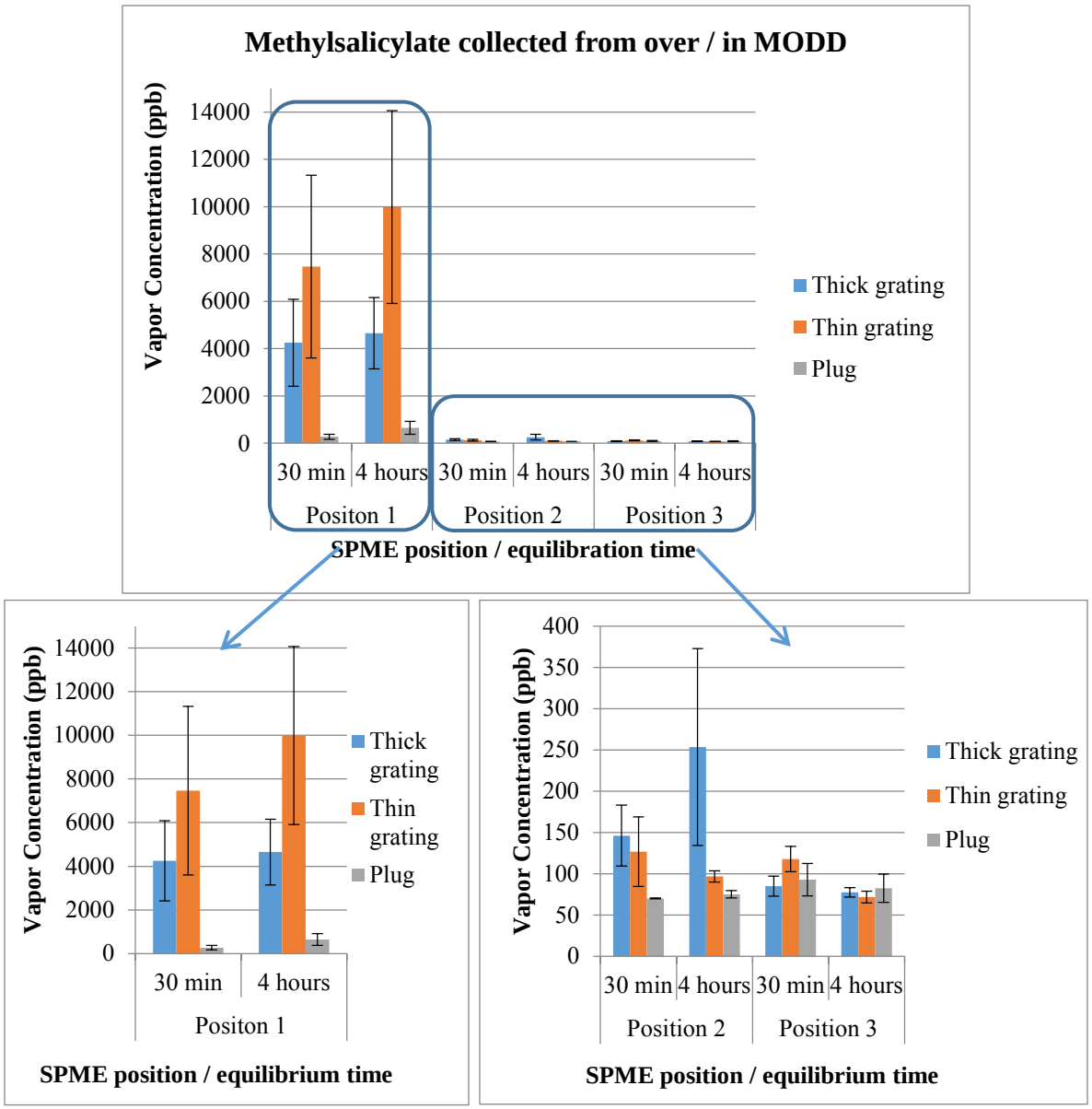

Figure 31. Vapor concentration of MeS in various location in the MODDs, taken by SPME with GC/MS analysis.

Discussion – Based on the comparisons of the variations of the MODD, it was apparent that the thinned grating compared to the original grating did not provide additional target odor at the outlet, and it is unlikely that it will improve canine detection. Canines will be more likely to detect target vapor from the MODD with no grating, but with the restrictor plug, as this configuration provides a greater concentration of vapor. Without either the plug or grating, too much vapor may enter the surrounding environment, whereby encompassing the entire space after a prolonged period of time. The plug prevents a great amount of odor from entering the environment, but also allows enough odor to reach the canine nose for olfaction. Three variations of restrictor plugs have been made with varying gap sizes. The greater the gap size, the greater the amount of vapor released. The plug with the largest gap size was used in this case. It could thus be deduced that smaller gap sizes would further reduce the amount of odor released if desired.

Final Canine Trials

Method - The goal of these evaluations was to assess the use of the MODD with binary HMEs, specifically AN with fuel oil. Using ammonium nitrate / fuel oil (ANFO) as the HME, the canines were asked to locate mixed and separated HME components held within the MODD. The proficiency of detection of mixed vs. separated material was compared.

Testing of the MODD was carried out using ANFO provided by Naval Surface Warfare Center Indian Head Explosive Ordnance Disposal Technology Division personnel. The mixed ANFO was comprised of prill AN (GFS Chemical) and diesel fuel (FO) (unknown source) at a 15:1 ratio. All ANFO used in the validation phase was contained in cotton bags (Pacific Midwest). ANFO as well as unmixed AN and FO components used in the MODD testing were placed into 22 mL PFA vials.

The trials were conducted at the Army Blossom Point Research Facility in Welcome, MD using 12 canines certified for explosive detection. Two canines were run on each day. All canines were previously trained on ANFO or were imprinted on the odor prior to testing. Canine information, including age, overall experience, and training experience with AN, is listed in Table 8. Canines from several agencies were used so specific training practices that might be unique to a specific agency would not influence the overall results. Particularly the canines' experience with AN alone as opposed to only in a mixture was noted.

Table 8. Canines participating in testing.

K9 ID	*Age (yrs)*	*Dog experience (yrs)*	*Team experience (yrs)*	*Experience with AN?*
1	5	3	3	In mixture only
2	7	5	0.5	In mixture only
3	4	2	2	In mixture only
4	5	4	1	In mixture only
5	5	4	0.5	In mixture only
6	7	5	0.5	In mixture only
7	4	2	2	In mixture only
8	8	6	0.5	In mixture only
9	3.5	2	2	Alone and in mixture
10	3	2	2	Alone and in mixture
11	10	9	9	Alone and in mixture
12	8	6	6	Alone and in mixture

Prior to MODD testing, validation runs were carried out to ensure that the canines could reliably detect ANFO hidden in various scenarios. Validation runs were conducted outdoors and consisted of lineups containing hidden target material (ANFO) and other distractors. Lineups included vehicles, gallon paint cans, and parcels (nylon bags), as well as a field search. 113 g (4 oz) of ANFO was used in the paint cans, and 226 g (8 oz) was used in the other scenarios. Distractors included empty vials, nitrile gloves and isopropyl wipes. The canines were expected to locate at least 90% of the targets with minimal false alarms prior to moving on to the MODD testing phase.

The MODD testing phase was held in a steel quanset hut containing furniture and equipment. Eleven MODDs (numbered one through 11) were used in total, and the contents of each MODD are given in Table 9. Each run utilized five MODDs total - four randomly selected MODDs containing blanks or distractors and one MODD containing a target odor (i.e. ANFO, AN and FO in separate vials, AN, or FO) or an additional blank. Distractors included cotton bags (similar to ones used to hold ANFO in validation runs), isopropanol wipes, and nitrile gloves. The blank/distractor MODDs were rotated throughout the testing. All material,

including distractors and targets, were enclosed in the MODDs for a minimum of 1.5 hours prior to testing.

Table 9. Contents of all MODDs used in canine trials, including targets, distractors, and blanks.

MODD #	Contents
1	Blank (contained clean vials only)
2	AN (3 vials x 1.88 g) and FO (0.36 g)
3	AN (3 vials x 1.88 g)
4	FO (0.36 g)
5	Blank (contained clean vials only)
6	Distractor - cotton bags
7	Blank (contained clean vials only)
8	Distractor - isopropanol wipes
9	ANFO (3 vials x 2 g)
10	Distractor - nitrile gloves
11	Blank (contained clean vials only)

This phase consisted of two sections. The first section was carried out to "acclimate" the canines to the MODD. For this section, the five MODDs were placed randomly near the center of the room, in plain sight (Figure 32). The canines were allowed to search all MODDs and give a final response if they detected a target. There were three scenarios, each including a MODD containing either ANFO, AN and FO separated, or no target (Table 10). The location of the target amongst the five MODDs was chosen using a random number generator and was changed for each canine. All MODDs were wiped with isopropanol wipes between runs.

Figure 32. Example of set up for canine trial. Canine in this picture is being "acclimated" to MODD with help of handler.

Table 10. Targets used in first section of MODD testing.

Scenario order	Target
1	ANFO
2	No target
3	AN and FO

In the second section of testing, the MODDs were concealed from view, hidden in various locations throughout the testing area. In all cases, MODDs were positioned in such a way that the odor was not blocked and could easily escape the device, and the canines were able to sniff at or very near the top of the device. Each canine was given five scenarios (Table 11). The order of the scenarios was previously chosen by a random number generator and was changed daily. The hiding locations were also changed for each scenario and the position of the target within a set of five locations was also chosen at random for each canine. All MODDs were wiped with isopropanol wipes between runs.

Table 11. Targets used in each testing scenario for the second section of MODD testing using hidden targets.

Scenario number	Target
1	AFNO
2	AN and FO
3	AN
4	FO
5	No target

Canines were allowed to work on or off lead, by discretion of the handler, with no time restriction. All testing was double-blind, meaning neither the canine/handler team nor the impartial assessor knew the correct location of the target. Canine/handlers waiting to be tested were not allowed to observe the testing to prevent "cheating". A positive response from a canine was identified by the handler. Canine "interest" in a target, distractor, or blank was noted by the handler and/or the assessor. After the canine either correctly located the target or thoroughly sampled all MODDs, the canine/handler was dismissed from the scenario.

Positive response rates to the mixed and unmixed ANFO were compared, as were positive response rates to ANFO and the individual components in the MODDs. False alert rates were considered by determining the positive predictive value (PPV), the probability that a positive response was correct by comparison to the rate of false positives (Eq. 2). A PPV significantly greater than 50% indicates that positive responses to the targets were not likely to

be by chance. A PPV calculation was previously used to assess the outcome of canine trials testing novel canine training aids [8].

$$PPV = \frac{True\ positive}{True\ postive+False\ positive} \quad \text{(Eq. 2)}$$

Results - All canines were first given a series of validation tests with mixed ANFO contained in cotton bags. Of the twelve canines tested, all but one passed the validation testing. The outcome from further testing with this canine was not included in the final results.

Canines were then allowed to search sets of five MODDS placed around the center of the room. This section was used to "acclimate" the canines to the device, and therefore the results were not reported. It was noted that canines with more experience on odor lineups tended to perform better on this section, compared to canines that were mainly trained to work in search scenarios. This did not affect the search section, as all canines were accustomed to searching for hidden target odors.

The results from the testing of the MODDs hidden throughout the test area are given in Table 12. The number of positive responses and false responses out of total number of responses was tallied. A positive response was considered an alert to target material (i.e. ANFO, AN+FO, AN or FO). A false response was considered an alert on any MODD containing material that was not a target (i.e. blanks or distractors). All responses, positive or false, were recorded by the assessor with concurrence from the handler. Interest in a target, blank, or distractor without a final response was noted by the assessor. Interest in a target material was included in red in Table 12.

Table 12. Results from canine testing on hidden MODDs. The number of positive responses and false responses out of the total possible number of responses are reported. Numbers in red indicate interest with no final response. *Canines did not perform last run of the day, which, in this case, was the scenario with no target.

		No Target	*ANFO*	*AN+FO*	*AN*	*FO*	*Comments*
K9 1	Pos. response	0/0	1/1	1/1	0/1	1/1	
	False response	0/5	0/4	1/4	0/4	0/4	
K9 2	Pos. response	n/a*	1/1	1/1	1/1	1/1	
	False response	n/a*	0/4	0/4	0/4	0/4	
K9 3	Pos. response	n/a*	1/1	1/1	0/1	0/1	
	False response	n/a*	0/4	0/4	2/4	1/4	
K9 5	Pos. response	0/0	1/1	1/1	0/1	0/1	Canine corrected from responding to all MODDs
	False response	4/5	0/4	0/4	0/4	2/4	
K9 6	Pos. response	0/0	1/1	1/1	0/1	1/1	Canine corrected from responding to all MODDs
	False response	3/5	1/4	0/4	2/4	2/4	
K9 7	Pos. response	0/0	0/1	1/1	0/1	0/1	
	False response	1/5	0/4	1/4	0/4	0/4	
K9 8	Pos. response	0/0	0/1	1/1	0/1	1/1	Canine responding to cotton bags --> corrected
	False response	0/5	2/4	1/4	0/4	1/4	
K9 9	Pos. response	0/0	1/1	1/1	1/1	0/1	Canine responding to cotton bags --> corrected
	False response	1/5	0/4	0/4	0/4	1/4	
K9 10	Pos. response	0/0	1/1	1/1	1/1	1/1	
	False response	0/5	0/4	0/4	0/4	0/4	
K9 11	Pos. response	0/0	1/1	1/1	0/1	1/1	Canine corrected from responding to all MODDs
	False response	3/5	0/4	0/4	0/4	0/4	
K9 12	Pos. response	0/0	1/1	1/1	1/1	1/1	Canine responding to nitrile gloves --> corrected
	False response	2/5	0/4	0/4	2/4	0/4	
Totals	**Pos. response**	**n/a**	**9/11**	**9(11)/11**	**3(4)/11**	**4(7)/11**	
	False response	**14/45**	**3/44**	**3/44**	**6/44**	**7/44**	
% of total	**Pos. response**	**n/a**	**82%**	**82%(100%)**	**27%(36%)**	**36%(64%)**	
	False response	**31%**	**6.8%**	**6.8%**	**14%**	**16%**	
Positive Predictive Value		***n/a***	***75%***	***75%***	***33%***	***36%***	

Nine out of 11 canines correctly alerted to both the ANFO and to the separated AN and FO placed in a single MODD (AN+FO). The same two canines that did not give a positive response to the mixed ANFO also did not alert on the AN+FO, thus the response rates were

identical. The PPV was calculated to be 75% for both the ANFO and AN+FO scenarios indicating that the rate of canine positive compared to false responses was significantly greater than chance.

It was observed that there were more false responses when no odor was recognized in the room (blank, AN, or FO scenarios). It appeared as though many of these false alerts were due to the canine "finding boxes" instead of locating a target odor. Once the behavior was recognized, it was corrected by the handler. Other false responses were on clean cotton bags similar to those used to contain ANFO in the validation runs, and clean nitrile gloves due to a previous encounter with training materials that had been exposed to nitrile gloves. These behaviors were also quickly extinguished by the handlers. There were far fewer false responses during the runs containing the target odors of ANFO or AN+FO.

Only 3 of the 11 canines positively responded to the AN material. Canines 1-8 had not been previously trained on AN alone, and thus did not give a positive response to that material. Canines 9-12 had all been previously trained on AN alone, and three of four of these canines gave an alert to the material indicating that only the canines trained on AN alone were proficient at locating the single component.

Four canines responded to the fuel oil. Due to the false response rate during this scenario, this was not significantly greater than chance (PPV = 36%). Several dogs showed clear interest in the fuel oil alone, but chose not to give the final response. It is possible that these canines recognized the similarity in the odor of the fuel oil alone compared to ANFO, but then acknowledged that it was not the same odor profile as the mixture and thus did not give a final response.

A chi-squared test was applied to compare the positive response rates of the canines to the ANFO (mixed or unmixed) to the individual components (AN alone or FO alone). There were a total of 7 positive responses to AN or FO and a total of 18 responses to ANFO (mixed and unmixed), thus $\chi^2 = 6.78$ and $\chi^2_{crit} = 3.84$ (based on a 95% confidence level and one degree of freedom), meaning there were significantly less positive responses to the individual components than to the ANFO. This indicates that most or all of the canines were locating the mixed odor and not the odor of one component or the other. These results support the previous research on canine detection of binary explosives [2] [4] [3].

Discussion - Evaluations of the MODD by explosive detecting canines were successful. The canines located the MODD containing the components of ANFO together at the same rate as when containing the mixed material; however canines located the MODDs containing only the single components at a significantly lower rate. These results indicate that the canines use the mixed odor profile of AN and FO together to locate ANFO, as opposed to using the odors from individual components, and that the canines recognized both ANFO, mixed and unmixed, in the MODD as the same or extremely similar odors.

CONCLUSIONS

It was shown that the Merger and MODD can accurately portray the odor of mixed explosives while housing the components separately. Analytical evaluations of the MODD demonstrated that the device successfully preserved the advantageous features of the previous state-of-the-art, the Merger, while providing a more compact design requiring a lower training material mass. Computational modeling and corresponding laboratory results have confirmed that the vapor distribution within the MODD provides a similar odor output as the Merger, though this is time dependent. Using separated surrogate compounds, as well as HME components, it was also shown that mixed odor is accurately represented for a number of separated compounds of varying functionalities, volatilities, and quantities. Results of canine trials using HME (ANFO) yielded no difference in detection proficiency for mixed vs. unmixed material in the MODD. These laboratory evaluations, in combination with the canine trials, provided a final MODD design that accurately portrayed the vapor profile of mixed explosive from separated odor components. The MODD can now be used to safely present binary explosive odor to canines for training.

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